

Volatilization Rates For Organic Chemicals Of Public Health Concern

**Prepared For
The Ontario Ministry of the Environment
Toronto, Ontario**

GORE & STORRIE LIMITED

1670 Bayview Avenue
Toronto, Ontario M4G 3C2

(416) 485-7715

March 1984

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CONSULTING ENGINEERS

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Water Resources Branch
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Attention: Mr. D.W. Draper
Mr. J.G. Ralston

Gentlemen:

Re: Volatilization Rates for Organic Chemicals
of Public Health Concern

We are pleased to submit our final report for the above project. We wish to thank the Ministry for giving us an opportunity to undertake this challenging assignment.

If you have any questions, please do not hesitate to contact our office.

All of which is respectfully submitted.

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Public Health & Water Quality Studies
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Water Resources Division

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EXECUTIVE SUMMARY

The volatilization of organic chemical compounds of public health concern from streams and rivers has been investigated. The volatilization rates are expressed in terms of liquid film coefficients (K_L). The main objectives of the study are: (1) To determine liquid film coefficients for ethylene gas using field data; (2) To develop relationships among liquid film coefficients, channel hydraulic parameters and properties of chemicals; and (3) To summarize relation between chemical structure and volatilization for organic compounds of concern in provincial streams and rivers.

Factors affecting volatilization of organic compounds, and conceptual models of transport across the air-water interface have been presented. The liquid film coefficients of ethylene are determined from data on ethylene and rhodamine WT dye distributions collected by the Water Resources Branch in the following streams and rivers:

- Avon River below Stratford Water Pollution Control Plant (WPCP)
- Baden Creek below Baden WPCP
- Grand River near Woolwich Township
- Nith River below Wellesley WPCP
- Speed River near Puslinch Township

The range of channel hydraulic parameters and liquid film coefficients of ethylene gas for the survey conditions in these streams are as follows:

- Discharge: 0.0453 - 7.29 m³/s
- Channel width: 3.11 - 38.6 m
- Average depth: 0.092 - 1.09 m
- Mean velocity: 0.028 - 0.27 m/s
- Channel bed slope: 0.069 - 0.635 m/km
- Liquid film coefficients of ethylene gas (K_L) : 0.97 - 8.07 m/day
- Temperature: 16° - 25°C

Relationships among K_L , channel hydraulic parameters and chemical properties were developed through statistical and dimensional analysis procedures. The relationships for K_L applicable to ethylene gas, given by

Equations 4.9 and 4.10 which are derived from dimensional analysis, have been found to provide better correlations with the observed K_L values. The computed values of K_L for ethylene gas for the above provincial streams are in the range 1.87 - 5.57 m/day from Equation 4.9, and 2.51 - 3.61 m/day from Equation 4.10. The parameters included in Equation 4.9 are width, depth, velocity, drop in height in a reach, density and viscosity of river water, and molecular diffusivity of ethylene gas, whereas Equation 4.10 includes depth, velocity, density, viscosity and diffusivity. A sensitivity analysis of various parameters appearing in Equations 4.7-4.10 has been carried out.

For other streams for which data are reported by Rathbun and Tai (1981), Equation 4.10 is found to overestimate the K_L values (by a factor of 3.53 on an average basis). The statistical relationship developed by Rathbun and Tai (1982) in which K_L is a function of depth, velocity and bed slope, has been found to underestimate K_L values for the above provincial streams and rivers (by an average factor of 0.75). These discrepancies are believed to be due to the effects of unaccountable factors such as wind velocity and presence of other chemicals in the rivers. It is suggested that the relationships derived from dimensional analysis are suitable to estimate K_L for ethylene gas in provincial streams and rivers. However, modifications of these relationships to include the effects of wind velocities is desirable, as data on these aspects become available.

An evaluation of the relations between K_L and molecular properties of volatile compounds has been carried out with the aid of theoretical review supplemented by experimental data reported in the literature. This evaluation has revealed that the relation between K_L and critical volume (or molecular diameter) is suitable to calculate K_L values for highly volatile organic chemicals (Henry's law constant $>10^{-3}$ atm-m³/mol) using the values for ethylene gas.

The computation of K_L for a given organic compound using the relationships developed herein is outlined in a step-by-step procedure. An example illustrates the various computations involved. In general, the method is applicable to volatile compounds with Henry's law constants greater than 10^{-3} atm-m³/mol.

The relationship between volatilization and chemical structure for a number of organic compounds has been evaluated based on the Henry's law constants (H). Compounds with H values $<10^{-7}$ atm-m³/mol are nonvolatile, 10^{-7} to 10^{-3} atm-m³/mol are moderately volatile and $>10^{-3}$ atm-m³/mol are highly volatile. The organic compounds of concern in the province have been grouped into a number of classes that are expected to behave similarly with respect to volatilization. Methods of computing Henry's law constants and molar and critical volumes for organic compounds have been presented.

SOMMAIRE

On a étudié la volatilisation des composés organiques présents dans les cours d'eau et qui posent des risques pour la santé publique. Les taux de volatilisation sont exprimés sous forme de coefficient de transfert de masse (K_L). Cette étude visait principalement : 1) à déterminer les coefficients de transfert de masse de l'éthylène à partir de données techniques; 2) à élaborer les relations entre les coefficients de transfert de masse, les paramètres hydrodynamiques des canaux (vitesse, profondeur et largeur du cours d'eau) et les propriétés des composés organiques; et 3) à établir les relations entre la structure chimique et la volatilisation des composés organiques qui constituent un danger pour la santé.

Le rapport présente les facteurs qui influent sur la volatilisation des composés organiques ainsi que la conceptualisation de leur transport dans l'interface air-eau. Les coefficients de transfert de masse de l'éthylène ont été déterminés à partir de données sur la distribution de l'éthylène et du colorant rhodamine WT qui ont été établies par la Direction des ressources atmosphériques pour les cours d'eau ci-après :

- rivière Avon, en aval de la station de dépollution de l'eau de Stratford
- ruisseau Baden, en aval de la station de Baden
- rivière Grand, près du canton de Woolwich
- rivière Nith, en aval de la station de Wellesley
- rivière Speed, près du canton de Puslinch

Les échelles des trois paramètres hydrodynamiques (vitesse, profondeur et largeur) et des coefficients de transfert de masse de l'éthylène au moment de l'étude étaient les suivantes :

Débit : 0,0453 - 7,29 m³/s
Largeur du cours d'eau : 3,11 - 38,6 m
Profondeur moyenne : 0,092 - 1,09 m
Vitesse moyenne : 0,028 - 0,27 m/s
Pente du canal : 0,069 - 0,635 m/km
Coefficients de transfert de masse de l'éthylène (K_L) :
0,97 - 8,07 m/jour
Température : 16° - 25 °C

Grâce à des analyses statistiques et dimensionnelles, on a pu élaborer les relations entre le K_L , les paramètres hydrodynamiques des canaux et les propriétés chimiques des composés organiques. Les relations entre le K_L et l'éthylène, dérivées des équations 4.9 et 4.10 -- résultant elles-mêmes d'une analyse dimensionnelle --, donnent de meilleures corrélations avec les valeurs observées du K_L . La valeur du K_L de l'éthylène dans les cours d'eau énumérés ci-dessus va de 1,87 à 5,57 m/jour avec l'équation 4.9 et de 2,51 à 3,61 m/jour pour l'équation 4.10. Dans l'équation 4.9, on a utilisé les paramètres

suivants : largeur, profondeur, vitesse, dénivellation du tronçon, densité et viscosité de l'eau ainsi que diffusion moléculaire de l'éthylène. Par contre, dans l'équation 4.10, on n'en a utilisé que cinq : profondeur, vitesse, densité, viscosité et diffusion moléculaire. De plus, une analyse de sensibilité de divers paramètres figurant dans les équations 4.7 à 4.10 a été effectuée.

Dans le cas des autres cours d'eau, mesurés par Rathbun et Tai en 1981, on a constaté que l'équation 4.10 exagérait les valeurs du K_L (d'un facteur de 3,53 en moyenne). Par ailleurs, le rapport statistique calculé par les mêmes auteurs en 1982, selon lequel le K_L est fonction de la profondeur, de la vitesse et de la pente du canal, sous-estime, d'un facteur moyen de 0,75, les valeurs du K_L pour les cours d'eau qui font l'objet de la présente étude. On croit que ces écarts sont causés par l'effet de facteurs non traités tels la vitesse du vent et la présence d'autres substances chimiques dans les cours d'eau. Il semble donc que les relations dérivées de l'analyse dimensionnelle permettraient d'estimer le K_L de l'éthylène dans les cours d'eau de la province. Cependant, il serait bon de les modifier en incorporant l'effet de la vitesse du vent, au fur et à mesure que l'on recueille les données à cet égard.

Une évaluation des relations entre le K_L et les propriétés moléculaires des composés organiques a été effectuée à l'aide d'un examen théorique et des résultats d'expérience qu'on a pu relever dans la documentation. Cette évaluation a révélé que la relation entre le K_L et le volume critique (ou diamètre moléculaire) permet de calculer les valeurs du K_L des composés organiques très volatils (constante de la loi de Henry $>10^{-3}$ atm-m³/mol) en utilisant les valeurs de l'éthylène.

Le calcul du K_L d'un composé organique donné à partir des relations élaborées dans la présente étude est décrit étape par étape. Un exemple précis illustre les différents calculs effectués. En général, il est possible d'appliquer la méthode de calcul aux composés organiques dont les constantes de la loi de Henry sont supérieures à 10^{-3} atm-m³/mol.

La relation entre la volatilisation et la structure chimique d'un certain nombre de composés organiques a été évaluée à l'aide des constantes de la loi de Henry (H). Des constantes H de $<10^{-7}$ atm-m³/mol représentent des composés non volatils; des constantes H de 10^{-7} à 10^{-3} atm-m³/mol, des composés modérément volatils; et des constantes de $>10^{-3}$ atm-m³/mol, des composés très volatils. Les composés organiques qui présentent un danger pour la santé publique en Ontario ont été regroupés en un certain nombre de classes, selon la façon dont ils réagiront probablement à la volatilisation. Par ailleurs, on présente ici les méthodes de calcul des constantes de la loi de Henry ainsi que les volumes molaire et critique des composés organiques.

RECOMMENDATIONS

During this investigation, several aspects related to development of predictive relationships for volatilization from water bodies were found to require further studies. Based on this knowledge, the following recommendations are made:

1. Development of modified relationships for K_L to include wind velocity (through dimensional analyses) is recommended.
2. An evaluation of the applicability of the relationships developed herein for chemical compounds other than ethylene is recommended as data become available.
3. It is recommended that field data gathering for volatilization studies include channel hydraulic parameters (discharge, width, depth, velocity and bed slope), and wind velocity measurements.
4. Investigation of relationships between K_L and molecular properties for chemical compounds with Henry's law constants lower than 10^{-3} atm-m³/mol (i.e., moderate and low volatile compounds) is also recommended.

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Constructive comments offered during the study by Messrs. Dennis W. Draper and John G. Ralston, Water Resources Branch, Ontario Ministry of the Environment, Toronto, are gratefully acknowledged. Thanks are due to Mr. Allan Bacchus for his help in making field data available for this study.

I INTRODUCTION

1.1 Background

Assessment of potential public health and other risks of organic chemicals in streams and rivers requires detailed evaluations of their transport, cycling and fate within the aquatic environment. Therefore, considerable importance is being given to gathering data on various physical, chemical and biological processes and factors related to these organic chemicals of public health concern. One of the important processes common to many of these organic compounds is volatilization. It is particularly necessary to know the volatilization rates of chemical compounds when dealing with emergency situations such as accidental spills of such compounds in order to predict the transport, fate and public health risks of the spills.

The volatilization process represents the physical transport of organic compounds through the water-air interface into the atmosphere. And, hence, there is a similarity between the widely-known atmospheric reaeration and the volatilization processes. Recently, Mackay and Yuen (1980) and Rathbun and Tai (1982) have shown that the volatilization rates applicable to organic compounds can be estimated from the field data gathered for the measurement of reaeration coefficients using dye and ethylene as tracers.

The Water Resources Branch of the Ontario Ministry of the Environment has conducted reaeration measurement studies in many streams and rivers using dye and ethylene. These data can thus be used to determine the volatilization rates applicable to streams and rivers. The field measurement technique is documented in the MOE publication Water Resources Paper 13 (A. Bacchus, 1981).

1.2 Volatilization Rate and Liquid Film Coefficient

Volatilization rate, also known as "desorption rate", is a coefficient which is analogous to the first-order rate coefficient, expressed in the units day^{-1} . The liquid film (or mass transfer) coefficient, which is a more fundamental quantity, is utilized in the expression for flux across the air-water interface (see Equation 2.1 in the next chapter); and it is expressed in the units m/day . The volatilization rate (K_v) and liquid film coefficient (K_L) are related by

$$K_L = L^* K_v \quad (1.1)$$

where L^* is a characteristic length, equal to the thickness of liquid film layer (see Section 2.2).

The thickness of the liquid film coefficient can be looked upon as being somewhat analogous to that for a boundary layer. In turbulent flow regimes normally encountered in natural streams and rivers, the boundary layer thickness is commonly defined as the magnitude of the normal distance from the boundary surface (i.e., channel bed) at which the velocity is equal to 99% of the surface velocity (Chow, 1959). Thus, for all practical purposes, the thickness can be approximated by the depth of water in the channel. Based on this analogy, the characteristic length, L^* , is set equal to the channel depth, Z ; such an approximation has been utilized by Rathbun and Tai (1981). Setting $L^*=Z$ in Equation 1.1, we get

$$K_L = ZK_v \quad (1.2)$$

In this investigation, K_L values are utilized in various analyses because of its fundamental nature.

1.3 Objectives

The main objectives of this study are as follows:

- (a) To determine mass transfer coefficients applicable to organic compounds of public health concern using the readily available data of ethylene and dye concentration distributions from provincial streams and rivers.
- (b) To develop relationships between mass transfer coefficients and bulk-flow characteristics of river channels which could be utilized to assess volatilization of organic compounds in other provincial streams and rivers.
- (c) To summarize relationships between chemical structure and volatilization for compounds of potential concern to the province.

II THEORETICAL BACKGROUND

2.1 Factors Affecting Volatilization

The volatilization of an organic compound from the water phase to the air phase is dependent on the physical and chemical properties of the compound, the presence of other chemical compounds, the hydrodynamic and other physical properties of the water body, and the physical properties of the atmosphere above the water surface (Liss and Slater, 1974; Mackay and Wolkoff, 1973; Lyman et al, 1982). These factors are presented below.

The physical and chemical properties of organic compounds affecting volatilization include molecular diameter, molecular weight, Henry's law constant and diffusion coefficient. The volatilization rates are also influenced by the presence of some modifying materials including adsorbents, electrolytes, emulsions and organic films (Mackay and Leinonen, 1975; Cohen et al, 1978).

The hydrodynamic and other physical properties of the river channel include flow rate, width, depth, velocity, bed slope, bed roughness, turbulence level and wind-induced currents. Factors such as suspended sediment concentration and the presence of other chemicals in the water phase could also affect volatilization.

The atmospheric properties of concern include wind speed, stability and other factors. Temperature affects the vapour pressure, and solubility, and thus, influences volatility of chemicals.

2.2 Theoretical Aspects

2.2.1 The Two-Film Theory:

Theoretical concepts of volatilization of chemical compounds from water to the atmosphere have been presented by various researchers (Lewis and Whitman, 1924; Mackay and Wolkoff, 1973; Liss and Slater, 1974; Mackay and Leinonen, 1975; Chiu and Freed, 1977 and 1979; Smith and Bomberger, 1979; Smith et al, 1980). A review of these theoretical approaches and their limitations have been presented in a recent publication (Lyman et al, 1982). The two-film theory of Lewis and Whitman (1924) is generally utilized to describe the volatilization of organic compounds

from water. The atmospheric reaeration in river channels is also described by the two-film theory. The salient aspects of the two-film theory are presented below.

The two-film model assumes that the bulk air and water phases are uniformly mixed, and that these two phases are separated by thin films of air and water, as shown schematically in Figure 2.1. The main resistance to gas transport is considered to exist in the liquid and gas phase interfacial layers (or films). Within these two films, the transport of the exchanging gas is assumed to take place by molecular diffusion. Then, application of the Fick's first law of diffusion for gas transport through each layer results in

$$F = k_L (C_{SL} - C_L) = k_g (C_g - C_{SG}) \quad (2.1)$$

where F is the flux of gas; k_L and k_g are the mass transfer coefficients for the liquid and gas phases, respectively (meters/day); C_L and C_g are the concentrations in the bulk liquid and gas phases, respectively; and C_{SL} and C_{SG} are the liquid-phase and gas-phase concentrations at the interface, respectively (see Figure 2.1). The mass transfer coefficients (also termed "exchange constants") are defined by the general relation

$$k = D_m / \delta \quad (2.2)$$

where D_m is the coefficient of molecular diffusion of gas in the appropriate layer of thickness δ (see Figure 2.1). The coefficients, k_L and k_g , are measures of the flux of gas per unit concentration gradient.

Following Cohen, et al (1978), the transport across the two-layer system (shown in Figure 2.1) can also be expressed as follows on the assumption that the concentrations immediately on either side of the interface are in equilibrium as expressed by a Henry's law constant (H):

$$F = K_L (C_L - C_S) \quad (2.3a)$$

$$\text{where } C_S = P_v / H \quad (2.3b)$$

$$\text{and } \frac{1}{K_L} = \frac{1}{k_L} + \frac{RT}{Hk_g} \quad (2.3c)$$

in which K_L is the overall mass transfer (or liquid film) coefficient based on the liquid phase (meters/day); R is the gas constant ($\text{atm. m}^3/\text{mol.K}$); T is the temperature ($^{\circ}\text{K}$); P_v is the atmospheric partial pressure (std. atm.);

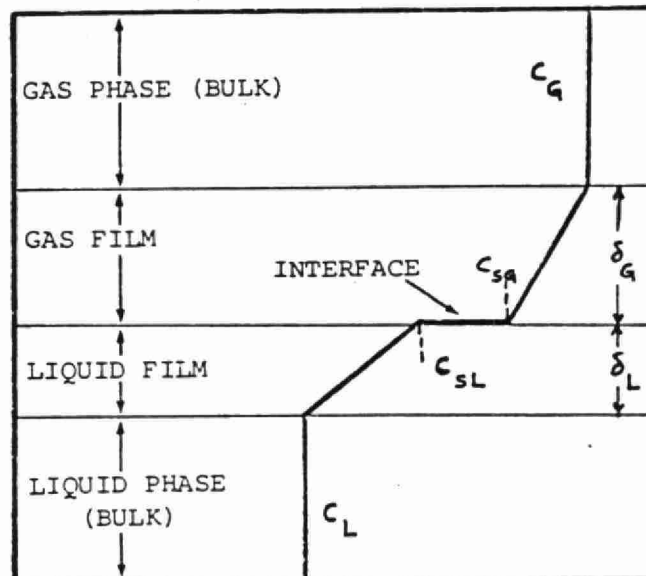


FIGURE 2.1 - SCHEMATIC REPRESENTATION OF TWO-FILM
GAS TRANSFER MODEL

and C_s is the concentration in the liquid phase in equilibrium with P_v (or saturation concentration).

The resistances to mass transfer are given by the reciprocals of the mass transfer coefficients. Therefore, Eq. 2.3 can be written as:

$$r_T = r_L + r_G \quad (2.4)$$

where r_T is the overall resistance; and r_L and r_G are the resistances offered by the liquid and gas films, respectively. Then, the fractions of the resistances to mass transfer in the liquid and gas films are given by

$$\frac{r_L}{r_T} = \frac{1}{1 + (r_G/r_L)} \quad (2.5a)$$

$$\frac{r_G}{r_T} = \frac{1}{1 + (r_L/r_G)} \quad (2.5b)$$

$$\text{where } r_L = \frac{1}{k_L} \quad (2.5c)$$

$$\text{and } r_G = RT/Hk_G \quad (2.5d)$$

Equations 2.5a-b can be utilized to determine the relative magnitudes of the resistances to mass transfer in the liquid and gas phases, respectively. The resistance may be dominant in either the liquid or the gas phase, or in both phases, depending on the relative magnitudes of k_L , k_G and H .

From Equation 2.5a, the smallest % of resistance in liquid film is seen to occur for the largest k_L and the smallest k_G . Using the reported maximum value of $k_L = 5.77$ m/day (from the data on benzene, chloroform, methylene chloride and toluene) and $k_G = 480$ m/day (based on evaporation of water in a canal), and correcting for the different molecules using the square root of inverse ratio of molecular weights, the % resistance in liquid film for ethylene and propane were found to be 99.69% and 99.91%, respectively, at 25°C (Rathbun and Tai, 1982). Based on this analysis, it has been concluded that the resistance to volatilization of ethylene and propane from water is mostly in the liquid film.

Rathbun and Tai (1982) have also evaluated the percentage of resistance in liquid film as a function of the Henry's law constant (H) by utilizing the data on k_L , k_G and H for organic compounds, reported in the literature (see Figure 2.2). Their results show that, for average conditions, more than 90% of the resistance is

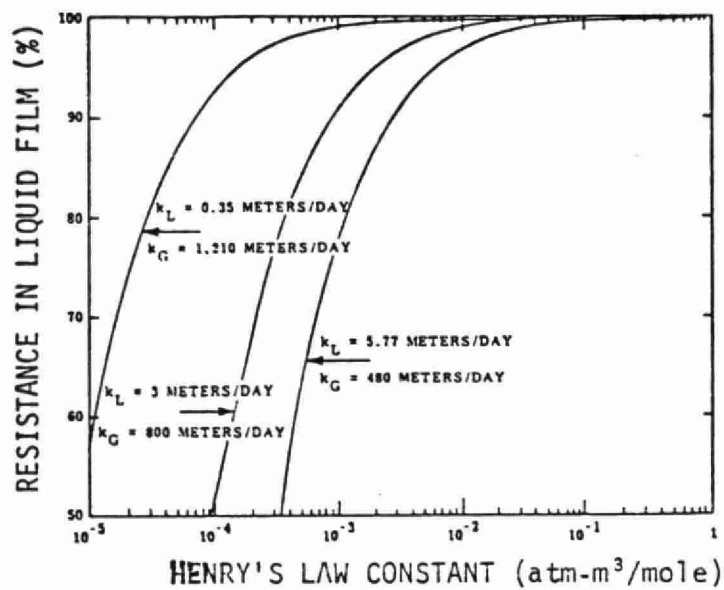


FIGURE 2.2 - RESISTANCE IN LIQUID FILM AS A FUNCTION
OF HENRY'S LAW CONSTANT
Source: Rathbun and Tai(1982)

in the liquid film for compounds with H values of about 10^{-3} at m. m³/g mole. Figure 2.2, developed by Rathbun and Tai (1982) can be utilized to determine the organic compounds which have volatilization characteristics similar to ethylene and propane. (Note: The Henry's law constants are discussed further in Chapter V).

2.2.2 Effects of Molecular Properties:

The molecular properties of chemical compounds which affect k_L values include molecular weight, molecular diameter and diffusivities.

The relationship of molecular weight M to k_L (or K_L for compounds with Henry's law constants greater than 10^{-3} atm m³/mol under average environmental conditions) can be expressed as

$$K_L \propto M^{-0.5} \quad (2.6)$$

The relationship of molecular diameter to K_L is usually expressed as

$$K_L \propto d_m^{-1} \quad (2.7)$$

where d_m refers to molecular diameter. Rathbun and Tai (1982 and references cited) report that molecular diameters were used successfully in some cases to adjust the K_L for a tracer gas to a value for organics. However, information on molecular diameters for organic compounds of interest is not readily available; and hence, molecular diameters are often estimated through the use of critical volumes and the longest dimension of a model of an organic compound. The adjustment of K_L values based on critical volumes is described in Chapter IV.

The liquid film coefficient has also been related to the molecular diffusivity of organic compounds in water by

$$K_L \propto D_m^n \quad (2.8)$$

where D_m is the molecular diffusion coefficient at a given temperature of river water, and n is an exponent. Rathbun and Tai (1981) utilized data on volatilization for a number of chlorinated hydrocarbons presented by Dilling (1977) in conjunction with D_m values calculated from an equation presented by Hayduk and Laudie (1974) to obtain a value of $n = 1.19$; however, the 95% confidence limits

were ± 0.64 . Roberts and Dandliker (1983) found $n = 0.66$ for six chlorinated and fluorinated hydrocarbons. Other works cited by Mackay and Yuen (1983) have found values of n to be 0.5 and 0.67.

Equations 2.6-2.8 can provide the basis for calculating the values of K_L for given organic compounds from the known values for tracers. Since M and d are basic properties of organic compounds, Equations 2.6 and 2.7 can be applied for adjusting the K_L values. However, the molecular diffusivity, D_m is dependent on the properties of river water as well as chemical compound; and hence Equation 2.8 may not adequately describe the effect of D_m on K_L . Thus, it is reasonable to conclude that Equations 2.6 and 2.7 are applicable for adjusting the K_L values of one compound to another whereas the effects of D_m on K_L need to be considered in a broader context in the analyses. The applicability of Equations 2.6 and 2.7 is dealt with further, in Chapter IV.

2.3 Review of Previous Studies

2.3.1 The Rathbun-Tai Relationships for Natural Streams:

Rathbun and Tai (1982) have correlated K_L values at 20°C for ethylene and propane with hydraulic data from eight streams and rivers. The total numbers of K_L values utilized in the analyses were 54 and 53 for ethylene and propane, respectively. Different forms of predictive equations were evaluated using the criterion of a normalized root-mean-square (RMS) error defined by:

$$E = \frac{100}{\overline{\ln K_L}_{\text{EXP}}} \sqrt{\sum \frac{(\ln K_L_{\text{EXP}} - \ln K_L_{\text{PRED}})^2}{n}} \quad (2.9)$$

where E = RMS error (%)

n = total number of data points

EXP and PRED = subscripts which refer to experimental and predicted values, respectively, and

$\overline{\ln K_L}_{\text{EXP}}$ = average value of the logarithms of the experimental K_L values

The $K_{L\text{EXP}}$ values ranged from 1.68 to 7.54 m/day for ethylene and 1.13 to 6.94 m/day for propane. The range of channel hydraulic parameters were as follows:

Discharge: 0.047 - 5.95 m³/s
 Depth: 0.101 - 0.555 m
 Velocity: 0.050 - 0.439 m/s
 Bed Slope: 0.0538 - 0.631 m/km

The correlation relationships of Rathbun and Tai (1982) are as follows:

$$\text{Ethylene: } K_L = 146 Z^{0.330} (\text{US})^{0.464} \quad (2.10)$$

$$\text{Propane: } K_L = 141 Z^{0.195} (\text{US})^{0.515} \quad (2.11)$$

The RMS errors (E) associated with Equations 2.10 and 2.11 were 25.6% and 34.8%, respectively. Since these relationships are empirical in nature, they are subject to limitations in their applicability to other streams and rivers, and for other organic compounds.

2.3.2 The Mackay-Yuen Laboratory Studies:

Mackay and Yuen (1983) measured volatilization rates of 11 organic compounds of varying Henry's law constants (5.57×10^{-6} to 5.18×10^{-3} atm. m³/mol at 20°C) in a wind-wave tank in the laboratory. The experiments were carried out at six different windspeeds in the range 5.96 - 13.2 m/s. From these studies, the following equations for K_L (m/day) are suggested:

$$K_L = 0.0864 + 294.624 (U_\star / \sqrt{S_{CL}}), (U_\star > 0.3) \quad (2.12)$$

$$K_L = 0.0864 + 1244.16 (U_\star^{2.2} / \sqrt{S_{CL}}), (U_\star < 0.03) \quad (2.13)$$

where U_\star = air side friction velocity (m/s), and

$$S_{CL} = \text{Schmidt Number} = \frac{\text{absolute viscosity}}{\text{diffusivity} \times \text{density}}$$

The value of U_* is obtained from

$$U_* = U_{10} (6.1 + 0.63U_{10})^{1/2} \quad (2.14)$$

where U_{10} is the windspeed at a height of 10 meters (m/s).

Equations 2.12 and 2.13 do not include such factors as depth and velocity of water; and hence, they have a limited scope for application to natural streams and rivers.

2.3.3 Relationships of Southworth:

Relationships between K_L , properties of chemical compounds, windspeed and water depths and currents have also been presented in a recent publication (Lyman et al, 1982). The equations for K_L (m/day) developed by Southworth (1979) are:

$$K_L = 5.64 \frac{U^{0.969}}{Z^{0.673}} \sqrt{\frac{32}{M}}, (U_w < 1.9 \text{ m/s}) \quad (2.15)$$

$$K_L = 5.64 \frac{U^{0.969}}{Z^{0.673}} \sqrt{\frac{32}{M}} \cdot \exp [0.526 (U_w - 1.9)], (1.9 < U_{wind} < 5 \text{ m/s}) \quad (2.16)$$

where M = molecular weight of organic compound (g/mole), and U_w = windspeed (m/s). While these relationships include depth, velocity, windspeed and molecular weight, they do not include other factors such as slope, viscosity and molecular diffusivity. Therefore, Equations 2.15 and 2.16 are also subject to some limitations in estimating liquid film coefficients for organic compounds.

III DATA COLLECTION AND ANALYSES

3.1 Liquid Film Coefficients from Tracer Studies

A modified tracer technique developed by Rathbun et al (1975) was utilized by the Ontario Ministry of the Environment to gather data in shallow streams and rivers. The details of this technique have been presented in the MOE publication Water Resources Paper No. 13 (Bacchus, 1981). In this technique, originally developed for direct measurement of atmospheric reaeration rates in streams, ethylene or propane gas and a conservative material (eg. rhodamine WT dye) are utilized as the tracers. The technique is based on the observation that the ratio between the rate of desorption of a tracer gas from water and the rate of absorption of oxygen by the same water remains constant regardless of the mixing conditions (Tsivoglou, 1967). The data gathered in these studies are also found to be useful to determine the volatilization rates applicable to organic compounds (eg. Rathbun and Tai, 1981 and 1982).

The field procedure adopted by the Ontario Ministry of the Environment involves simultaneous injection of ethylene gas and rhodamine WT dye solution (as a line source across the channel) for a known duration of time at the head of a study stretch of river channel, and monitoring for dye and ethylene gas concentrations as a function of time at selected downstream stations as the plume passes those stations. These data are utilized to calculate the volatilization (or desorption) coefficient (K_v) for a channel reach using the relationship:

$$K_v = \frac{1}{t} \ln \left\{ \frac{(c_g/c_d)_{us}}{(c_g/c_d)_{ds}} \right\} \quad (3.1)$$

where c_g and c_d = concentration of ethylene gas and dye, respectively;

us and ds = subscripts denoting upstream and downstream stations, respectively;

t = travel time in the reach (days)

K_v = desorption coefficient of ethylene gas (day^{-1})

referred to base e at the average river water temperature.

The liquid film coefficient for ethylene gas in each reach is then determined from the equation (Rathbun and Tai, 1981)

$$K_L = K_V Z$$

(3.2)

where Z is the average depth of flow in the channel reach (meters), and K_L is the liquid film coefficient for ethylene gas (meters/day). The K_L values will be utilized to develop relationships of K_L to bulk flow characteristics of river channels and properties of organic compounds.

3.2 Study Areas and Hydraulic Characteristics of River Channels

Data from the following streams and rivers, gathered by the Water Resources Branch, Ontario Ministry of the Environment, were analyzed to determine the liquid film coefficients:

- Avon River below the Stratford Water Pollution Control Plant (WPCP)
- Baden Creek below Baden WPCP
- Grand River near Woolwich Township, Waterloo County (Close to Winterborne)
- Nith River below Wellesley WPCP
- Speed River near the Township of Puslinch downstream from Guelph

Figure 3.1 shows the layouts of the various study segments of the rivers and streams. Three surveys were carried out in the Grand and Speed rivers and one survey was conducted in each of the other streams.

The field survey dates for various streams and the salient hydraulic characteristics of the stream channels are presented in Table 3.1. Generally, the stream channels are very shallow, the channel bed being composed mostly of rocks, pebbles and sand. The ranges of hydraulic parameters of the streams are as follows:

Discharge (Q):	0.0453 - 7.29 m ³ /s
Reach length (L):	127.5 - 2555.0 m
Channel width (B):	3.11 - 38.6 m
Average depth (Z):	0.092 - 1.09 m
Mean velocity (U):	0.028 - 0.27 m/s (2,419.2 - 23,328.0 m/day)
Channel bed slope (S):	0.069 - 0.0635 m/km (0.00069 - 0.00635 m/m)

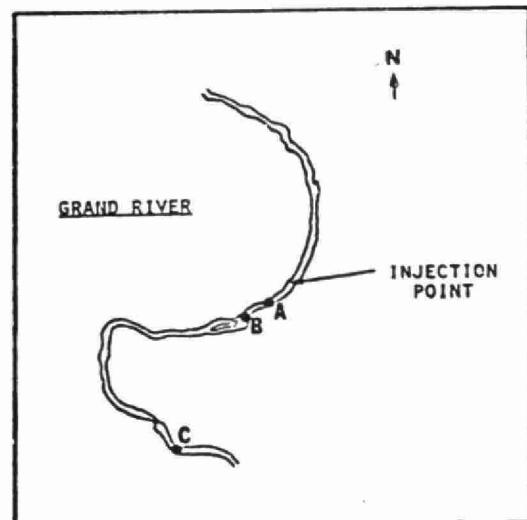
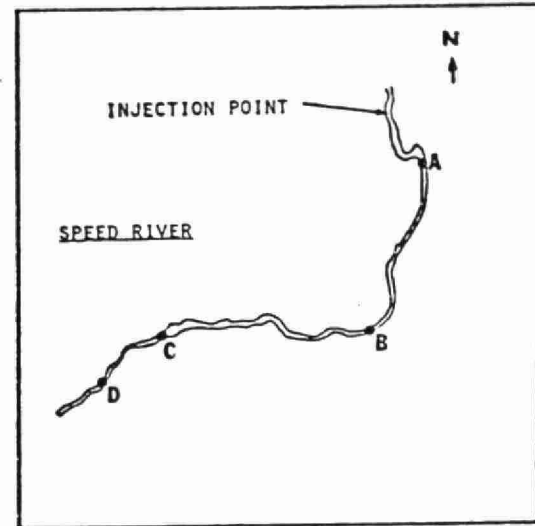
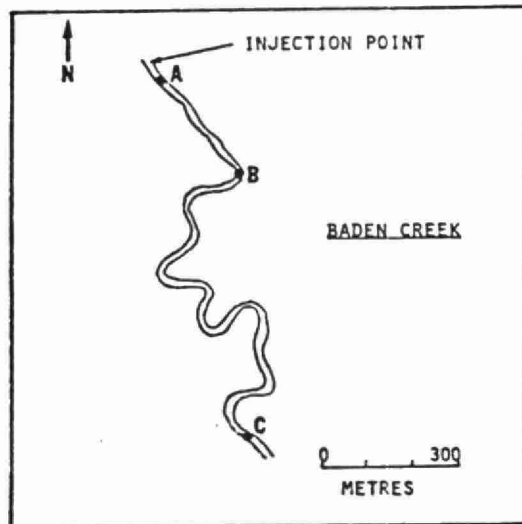
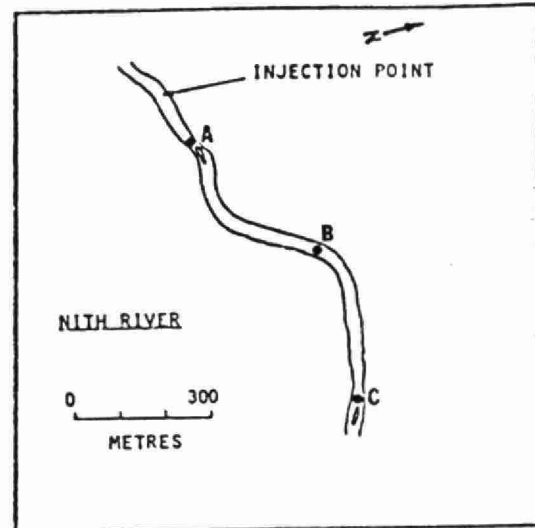
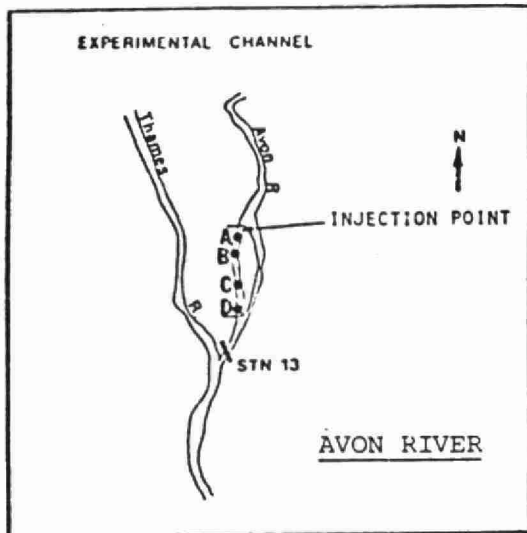


FIGURE 3.1 - SCHEMATIC DIAGRAMS OF STREAM AND RIVER SEGMENTS

TABLE 3.1
SUMMARY OF CHANNEL HYDRAULIC DATA

STREAM	SURVEY DATE	REACH	L (m)	Q (m ³ /s)	B (m)	Z (m)	U (m/d)	S (m/m)
AVON R.	9/04/80	BC	148.00	0.110	7.31	0.108	12009.6	0.0034
		CD	127.25	0.110	7.23	0.092	14256.0	0.0034
BADEN CR.	7/27/77	BC	274.00	0.045	3.11	0.118	10627.2	0.0063
		CD	1180.00	0.045	3.47	0.236	4752.0	0.0063
GRAND R.	6/02/78	AC	2555.00	4.090	29.47	0.680	17280.0	0.0013
GRAND R.	7/11/78	AB	115.00	4.270	29.69	0.685	18144.0	0.0013
		BC	2240.00	4.270	29.69	0.685	18144.0	0.0013
		AC	2555.00	4.270	29.69	0.685	18144.0	0.0013
GRAND R.	8/23/78	BC	2440.00	7.290	34.18	0.790	23328.0	0.0013
NITH R.	8/03/77	AB	303.00	0.153	17.91	0.305	2419.2	0.0006
		BC	260.00	0.153	13.80	0.264	3628.8	0.0006
SPEED R.	6/07/78	AB	1480.00	3.360	30.68	1.090	8726.4	0.0011
		BC	1720.00	3.360	38.60	0.440	17280.0	0.0011
		CD	650.00	3.360	38.60	0.440	17280.0	0.0011
		BD	2380.00	3.360	38.60	0.440	17280.0	0.0011
SPEED R.	8/10/78	AB	1480.00	2.120	29.84	0.890	6998.4	0.0011
		BC	1720.00	2.120	38.60	0.403	12009.6	0.0011
SPEED R.	8/24/78	AB	1480.00	2.430	30.09	0.943	7430.4	0.0011
		BC	1720.00	2.430	38.60	0.414	13392.0	0.0011
		CD	650.00	2.430	38.60	0.414	13392.0	0.0011
		BD	2380.00	2.430	38.60	0.414	13392.0	0.0011

An evaluation of the readily available channel hydraulic data showed that the channel widths, depths and velocities for the following survey conditions were identical (see Table 3.1):

Grand River, June 11, 1978 - Reaches AB and BC

Speed River, June 7, 1978 - Reaches BC and CD

Speed River, August 24, 1978 - Reaches BC and CD

Therefore, in these three cases, the two successive reaches were combined into one reach (i.e., Grand River - Reach AC; and Speed River - Reach BD). The hydraulic characteristics for these cases are given in Table 3.1 for the individual, as well as the combined reaches.

Data on channel bed slopes were obtained from topographic maps. However, the slopes for individual reaches could not be determined from these maps. In the analyses, the drop in height within each reach, given by (reach length times the slope), will be utilized.

3.3 Calculation of Liquid Film Coefficients for Ethylene Gas

The data analyses were carried out with the aid of the computer program HGREDYET, documented in the Water Resources Paper No. 13 (Bacchus, 1981). The program output includes reaeration rates (K_a per day) at the river water temperature, $T^\circ\text{C}$, and at 20°C , calculated from Equation 3.1. These were converted to volatilization rates (K_v), using the relationship:

$$K_v = 0.89 K_a \quad (3.3)$$

where the value 0.89 is the ratio of the desorption coefficient for ethylene gas to the absorption coefficient for oxygen (Rathbun et al, 1975). The liquid film coefficients (K_L) at the average instream temperature ($T^\circ\text{C}$) were then calculated from Equation 3.2. The results are tabulated in Table 3.2. The values of K_L for the study reaches of various streams and rivers are seen to range from 0.97 to 8.07 meters/day. The river water temperatures in various streams ranged from 16° to 25°C . It should be noted that the data for the Grand

River - June 11, 1978, and Speed River - June 7, and August 24, 1978, surveys include the K_L values for the individual reaches as well as the combined reaches stated in the previous section.

The values of K_L at 20°C are also presented in Table 3.2. These are utilized in the multiple regression analysis described in the next chapter.

3.4 Other Data

The development of relationships between K_L and the channel hydraulic parameters, presented in the following chapter, requires data on densities and viscosities of stream waters as well as molecular diffusion coefficient of ethylene gas (D_m) for the instream temperature conditions. The densities (ρ) and absolute viscosities (μ) were obtained from the CRC Handbook of Chemistry and Physics (1980). The diffusion coefficients were computed from the following equation (Hayduk and Laudie, 1974; Lyman et al, 1982):

$$D_m = \frac{13.26 \times 10^{-5}}{\mu^{1.14} V_B^{0.589}} \quad (3.4)$$

where D_m is the molecular diffusion coefficient of ethylene gas (cm^2/sec);
 μ is the absolute viscosity of water (centipoise or 10^{-2} g/cm sec);
and V_B is the molar volume of ethylene gas computed by the LeBas method, outlined in Chapter V, ($V_B = 44.4 \text{ cm}^3/\text{mol}$). The values of D_m (in cm^2/sec) obtained from Equation 3.4, have been converted to the units (m^2/day). The values of density, absolute viscosity and molecular diffusion coefficient are given in Table 3.2.

TABLE 3.2
VISCOSITY, DENSITY, DIFFUSIVITY AND LIQUID FILM COEFFICIENTS

STREAM	SURVEY DATE	REACH	T (°C)	μ (Kg/m-day)	ρ (Kg/m ³)	D_m (m ² /day)	K_L @T°C (m/day)	K_L @20°C (m/day)
AVON R.	9/04/80	BC	20.7	90.74	998.0559	0.000116	2.66	2.61
		CD	20.7	90.74	998.0559	0.000116	2.39	2.35
BADEN CR.	7/27/77	BC	25.0	76.90	997.0448	0.000140	3.57	3.17
		CD	25.0	76.90	997.0448	0.000140	3.04	2.70
GRAND R.	6/02/78	AC	19.0	88.73	998.4052	0.000119	1.80	1.84
GRAND R.	7/11/78	AB	17.0	93.40	998.7748	0.000112	8.30	8.92
		BC	17.0	93.40	998.7748	0.000112	4.29	4.60
		AC	17.0	93.40	998.7748	0.000112	4.64	4.98
GRAND R.	8/23/78	BC	22.0	82.50	997.7704	0.000129	8.07	7.69
NITH R.	8/03/77	AB	25.0	76.93	997.0448	0.000140	2.63	2.33
		BC	25.0	76.93	997.0448	0.000140	2.26	2.01
SPEED R.	6/07/78	AB	16.0	95.82	998.9430	0.000109	0.97	1.07
		BC	16.0	95.82	998.9430	0.000109	3.81	4.19
		CD	16.0	95.82	998.9430	0.000109	1.95	2.14
		BD	16.0	95.82	998.9430	0.000109	3.01	3.31
SPEED R.	8/10/78	AB	16.7	94.12	998.8252	0.000111	3.10	3.35
		BC	16.7	94.12	998.8252	0.000111	3.74	4.05
SPEED R.	8/24/78	AB	19.0	88.73	998.4052	0.000119	5.73	5.87
		BC	19.0	88.73	998.4052	0.000119	3.31	3.39
		CD	19.0	88.73	998.4052	0.000119	5.27	5.39
		BD	19.0	88.73	998.4052	0.000119	4.33	4.44

IV DEVELOPMENT OF PREDICTIVE RELATIONSHIPS

4.1 General Approach

In order to develop relationships between the liquid film coefficient (K_L) and the channel hydraulic parameters, two approaches have been utilized. The first approach is a multiple regression analysis and the second approach is a dimensional analysis using the Buckingham Π -theorem. The regression analysis is mainly intended as an attempt to identify the most significant channel hydraulic parameters affecting K_L . These regression analysis results will likely aid in selecting the parameters for the dimensional analysis.

4.2 Relationships from Multiple Regression Analysis

For multiple regression analyses, the functional relationships between K_L and the channel hydraulic parameters were considered to be of the general forms:

$$K_L = a_0 B^{a_1} Z^{a_2} U^{a_3} (LS)^{a_4} \quad (4.1)$$

$$K_L = a_0 Z^{a_2} (US)^{a_5} \quad (4.2)$$

where K_L = liquid film coefficient of ethylene gas at 20°C (m/day)
 B = channel width (m)
 Z = average depth (m)
 U = mean velocity (m/day)
 L = length of reach (m)
 S = channel bed slope (m/m)
 (LS) = drop in height in reach (m)
 a_0 to a_5 = regression coefficients

It should be noted that the general form of Equation 4.2 is similar to Equation 2.10 obtained by Rathbun and Tai (1982).

Equations 4.1 and 4.2 were linearized by taking logarithms on both sides. The computer program RLSEP, available in the IMSL package, was utilized to obtain regression models using a forward stepwise algorithm. The results of the multiple regression analyses, summarized in Table 4.1, show that the variation explained is in the range 6.8 - 22.4%, whereas the residual standard deviations expressed as a %

TABLE 4.1

SUMMARY OF MULTIPLE REGRESSION ANALYSES

RUN NO.	REGRESSION EQUATION	REGRESSION COEFFICIENTS	% VARIATION EXPLAINED	RESIDUAL STD. DEV. AS A % OF RESPONSE MEAN	OVERALL F-VALUE
1	$K_L = a_0 B^{a_1}$	$a_0 = 2.02$ $a_1 = 0.15$	6.8	44.3	0.94
2	$K_L = a_0 Z^{a_2}$	$a_0 = 3.45$ $a_2 = 0.12$	3.7	45.0	0.50
3	$K_L = a_0 U^{a_3}$	$a_0 = 0.21$ $a_3 = 0.3$	14.4	42.4	2.20
4	$K_L = a_0 (LS)^{a_4}$	$a_0 = 2.90$ $a_4 = 0.46$	13.2	42.7	2.00
5	$K_L = a_0 U^{a_3} (LS)^{a_4}$	$a_0 = 0.46$ $a_3 = 0.20$ $a_4 = 0.10$	18.1	43.2	1.32
6	$K_L = a_0 Z^{a_2} U^{a_3} (LS)^{a_4}$	$a_0 = 0.45$ $a_2 = 0.05$ $a_3 = 0.21$ $a_4 = 0.08$	18.6	45.0	0.84
7	$K_L = a_0 B^{a_1} Z^{a_2} U^{a_3} (LS)^{a_4}$	$a_0 = 0.65$ $a_1 = 0.25$ $a_2 = -0.21$ $a_3 = 0.06$ $a_4 = 0.18$	22.4	46.1	0.72
8	$K_L = a_0 Z^{a_2} (US)^{a_5}$	$a_0 = 2.42$ $a_2 = 0.19$ $a_5 = 0.15$	12.9	44.5	0.89

of response mean (i.e., % variation not explained) range from 42.4 to 46.1%. The latter statistic is the same as the RMS error (Equation 2.9) which was utilized as the criterion for selecting the regression models by Rathbun and Tai (1982). The results for run #7 (having the higher % variation explained) suggest that K_L is likely a function of B, Z, U and (LS). However, the variation not explained by the regression model (Equation 4.1) is also quite high (46.1%), indicating the possible effect of other factors such as diffusivity and viscosity. It should be noted that the analyses presented in this section are referred to the temperature of 20°C.

The results for run #8 show the fit of Equation 4.2 to the data. These results are seen to differ from the relationship for ethylene (Equation 2.10) obtained by Rathbun and Tai (1982).

Table 4.1 also gives the F-statistic values (indicative of significance levels) for various regression equations. In general, the values are lower than 2.2 indicating that they are significant at levels of about 15% and higher. The results for the runs 5-7 show an increase in the % variation explained as the number of dependent variables is increased; however, there is also an increase in the variation not explained, accompanied by a decrease in the overall F-values. These results suggest a somewhat weak statistical correlation of K_L to the channel bulk flow parameters.

In a relative sense, the parameters U, LS, B and Z are important in that order (based on the overall F-values and % variation explained). Since the values of slopes are taken to be the same for successive reaches for some of the streams (because of the nature of the data available), the significance of the term (LS) may not be discernible from this analysis. This regression analysis suggests that for dimensional analysis, it is desirable to consider all the four parameters.

4.3 Relationships from Dimensional Analysis

Dimensional analysis is a means of developing relationships between dependent and independent variable parameters in hydraulic transport studies. It involves a systematic organization of the variable parameters into the smallest number of significant dimensionless parametric groups. Such an organization is facilitated by the fact that a mathematical relationship must be dimensionally homogeneous; in other words, each term in an equation, when reduced to the basic dimensions of

length, time and mass (or force), must contain identical powers of each of the respective dimensions. Thus, if the variables to be included in the relationship are known, then these variables should occur in the relationship so as to attain dimensional homogeneity. The principal tool of dimensional analysis is known as the Buckingham Π -theorem (Rouse, 1961).

The variable parameters which can be considered in this dimensional analysis are as follows:

- liquid film coefficient at a given temperature of river water
- width, depth, velocity and drop in height in a reach of stream channel
- acceleration due to gravity
- density of water at the given temperature of river water
- absolute viscosity of water at the water temperature
- molecular diffusivity of organic compound in river water
- wind velocity

The molecular weight and molecular diameter are not included in the dimensional analysis since these two parameters represent the properties of organic compounds, as stated earlier (see Chapter II). Also, data on wind velocities for the field survey conditions outlined in Chapter III, are not readily available; and hence, wind velocity will be ignored in this analysis. It should be noted that this analysis is specific to the tracer gas under consideration, (i.e., ethylene gas). However, the liquid film coefficient, density, viscosity and diffusion coefficient at the average instream temperature will be considered in order to retain the generality of the relationship. Thus, the general relationship can be written as

$$K_L = f(B, Z, U, LS, g, \rho, \mu, D_m) \quad (4.3)$$

where K_L = liquid film coefficient

B = channel width

Z = average depth

U = mean velocity

LS = drop in height

L = length of reach

S = bed slope

g = acceleration due to gravity

ρ = density of water at $T^{\circ}\text{C}$
 μ = absolute viscosity of water
 D_m = molecular diffusivity of organic compound

Because of the mathematical equilibrium between the independent variable (K_L) and the dependent variables appearing on the right hand side of Equation 4.3, the variables can be grouped in another functional relationship equal to zero:

$$f'(K_L, B, Z, U, LS, g, \rho, \mu, D_m) = 0 \quad (4.4)$$

Then, according to the Buckingham Π -Theorem (Rouse, 1961), these nine variables can be grouped into $(9-3) = 6$ dimensionless Π -terms since each variable can be described by the three fundamental dimensional units mass, length and time as follows:

$$\phi = (\Pi_1, \Pi_2, \dots, \Pi_6) = 0 \quad (4.5)$$

Each Π -term will have four variables, only one of which need be changed from one term to another.

Numerous combinations of the parameters into the six dimensionless Π -terms are possible. For this analysis, a number of different combinations were attempted. Correlations of the data to these relationships resulted in varying degrees of variation explained (approximately 3-66%). Based on these detailed analyses, the following dimensionless relationship has been selected:

$$\left(\frac{K_L}{U}\right) = a_0 \left(\frac{B}{Z}\right)^{a_1} \left(\frac{LS}{Z}\right)^{a_2} \left(\frac{\rho U Z}{\mu}\right)^{a_3} \left(\frac{g Z}{U^2}\right)^{a_4} \left(\frac{U Z}{D_m}\right)^{a_5} \quad (4.6)$$

in which a_0 is a numerical constant (dimensionless), and $a_1 - a_5$ are the exponents of the individual dimensionless groups. The ratio of absolute viscosity to density (i.e., μ/ρ) is equal to the kinematic viscosity (ν). Each dimensionless term appearing on the right hand side is related to a characteristic property affecting K_L , as follows:

$\frac{B}{Z}$ = Aspect ratio of channel

$\frac{LS}{Z}$ = Ratio of drop in height to channel depth

$\frac{UZ}{\nu}$ = R_N = Reynolds number of flow indicative of viscous effects

$\frac{u^2}{gZ}$ = F = Froude number denoting gravitational effects

$\frac{UZ}{D_m} = \left(\frac{UZ}{\nu}\right)\left(\frac{\nu}{D_m}\right) = R_N S_{CL}$ = product of Reynolds (R_N) and Schmidt (S_{CL}) numbers

Equation 4.6 is linearized by taking logarithms on both sides. The values of various dimensionless terms were calculated by using the data summarized in Tables 3.1 and 3.2 (see Chapter III). The IMSL routine RLSEP was utilized to determine the regression coefficients $a_0 - a_5$. From this procedure, the following relationship is obtained:

$$\frac{K_L}{U} = 2.7 \left(\frac{B}{Z}\right)^{0.14} \left(\frac{LS}{Z}\right)^{0.16} \left(\frac{UZ}{\nu}\right)^{1.85} \left(\frac{u^2}{gZ}\right)^{0.35} \left(\frac{UZ}{D_m}\right)^{-1.89} \quad (4.7)$$

The various statistical parameters associated with this correlation relationship are as given below:

Variation explained by the fit	= 66.6%
RMS error (defined by Equation 2.9)	= 6.2%
Overall F-value	= 3.59
Significance level	= 4.6%

These statistical characteristics of the regression fit indicate that Equation 4.7 satisfactorily describes the functional relationship between K_L and the channel bulk flow parameters and chemical characteristics for the range of data presented in Tables 3.1 and 3.2.

The F-statistic values associated with individual dimensionless terms were in the range 0.56 - 4.73. The F-values for the last three terms of Equation 4.6 were significant in the range 6 - 13% whereas, the significance levels for the first two terms exceeded 20%. Therefore, a regression fit was carried out by considering the last three terms of Equation 4.6, to obtain the following relationship:

$$\frac{K_L}{U} = 7.16 \left(\frac{UZ}{\nu} \right)^{1.51} \left(\frac{U^2}{gZ} \right)^{-0.23} \left(\frac{UZ}{D_m} \right)^{-1.59} \quad (4.8)$$

The statistical characteristics of the regression fit are as follows:

Variation explained	= 62.14%
RMS error (defined by Equation 2.9)	= 5.94%
Overall F-value	= 6.02
Significance level	= 1.1%

The F-values associated with the individual terms were in the range 2.44 - 6.18 which correspond to significance levels of 3-5% approximately. Thus, Equation 4.8 also appears to describe the functional relationship satisfactorily. This relationship can be utilized when data on channel slopes are not readily available.

Equations 4.7 and 4.8 can be simplified to obtain the following relationships:

$$K_L = 2.70 \ g^{0.35} \ \nu^{-1.85} \ D_m^{1.89} \ B^{0.4} \ Z^{-0.25} \ U^{0.26} \ (LS)^{0.16} \quad (4.9)$$

$$K_L = 7.16 \ g^{0.23} \ \nu^{-1.51} \ D_m^{1.59} \ Z^{0.15} \ U^{0.46} \quad (4.10)$$

where $\nu = \mu/\rho$ is the kinematic viscosity of water at the instream temperature

According to Equation 4.9, K_L would decrease with an increase in depth whereas Equation 4.10 indicates K_L increasing with depth. Based on the known relationships of reaeration coefficient to channel hydraulic parameters, the exchange rates at the air-water interface tend to decrease with increasing depths (due to lower turbulence levels) and vice versa. Thus, it is thought that Equation 4.9 is superior to Equation 4.10.

Equations 4.7 to 4.10 are dimensionally homogeneous, and hence, the units of K_L are dependent on the units of various parameters appearing on the right hand side. For example, if the various parameters are in the gram-meter-second units, then K_L is in meters/second. Note that these relationships are specifically valid to estimate K_L for ethylene gas at a given temperature.

4.4 Evaluation of Predictive Relationships

In this section, the predictive capabilities of Equations 4.9 and 4.10 will be evaluated by a comparison with the observations presented in Chapter III (for streams and rivers in Ontario) and the data presented by Rathbun and Tai (1981). An evaluation of the applicability of Equation 2.10 of Rathbun and Tai (1982) to the provincial streams and rivers will also be carried out. The relationships for K_L developed by Mackay and Yuen (1983) and Southworth (1979), presented in Chapter II, could not be evaluated because of a lack of appropriate data.

Equations 4.9 and 4.10 have been utilized to compute the values of K_L for ethylene gas for the streams and rivers listed earlier (see Table 3.1). The computed values of K_L are presented in Table 4.2 along with the observed K_L values (range of observed K_L : 0.97 - 8.07 m/day). The values obtained from Equation 4.9 are in the range 1.87 - 5.57 m/day, whereas Equation 4.10 gives values in the range of 2.51 - 6.31 m/day. Figures 4.1 and 4.2 show plots of the K_L values computed from Equations 4.9 and 4.10 versus the observed K_L values. The average K_L values are 3.46 m/day for the observations, and 3.03 and 3.28 m/day from Equations 4.9 and 4.10, respectively. The ratios (predicted K_L /observed K_L) vary from 0.44 to 2.11 with Equation 4.9, and 0.51 to 2.64 with Equation 4.10; and the average ratios are 1.01 and 1.12 for Equations 4.9 and 4.10, respectively. These results indicate that the predictions of Equations 4.9 and 4.10 compare favourably with the observations. On an overall basis, Equation 4.9 is slightly better than Equation 4.10.

The values of K_L for ethylene gas, computed from Equation 2.10 of Rathbun and Tai (1982), are presented in Table 4.2. The computed values (K_{LC}) are in the range 0.74 - 3.44 m/day. Figure 4.3 shows a plot of the computed versus observed K_L values. Generally, the computed values are seen to be lower than the observations; the averages of computed and observed values are 2.1 and 3.46 m/day, respectively. The predicted values range from 0.34 to 2.27 times the observed values, the average ratio being 0.75 (see Table 4.2). These results show that Equation 2.10 developed by Rathbun and Tai (1982) generally underestimates the K_L values for the provincial streams and rivers.

TABLE 4.2
COMPARISON OF OBSERVED AND COMPUTED K_L FOR ONTARIO STREAMS

OBSERVED K_L (m/day)	EQUATION 4.9		EQUATION 4.10		EQUATION 2.10	
	K_{LC}	K_{LC}	K_{LC}	K_{LC}	K_{LC}	K_{LC}
	(m/day)	K_L	(m/day)	K_L	(m/day)	K_L
2.66	2.10	0.79	2.51	0.95	2.01	0.75
2.39	2.22	0.93	2.66	1.11	2.06	0.86
3.57	3.34	0.94	4.17	1.17	2.61	0.73
3.04	3.01	0.99	3.19	1.05	2.26	0.74
1.80	3.80	2.11	4.22	2.35	2.85	1.58
4.64	3.14	0.68	3.65	0.79	2.92	0.63
8.07	5.57	0.69	6.31	0.78	3.44	0.43
2.63	2.57	0.98	2.43	0.92	0.64	0.24
2.26	2.60	1.15	2.86	1.27	0.74	0.33
0.97	1.87	1.93	2.57	2.64	2.20	2.27
3.01	3.32	1.10	3.07	1.02	2.24	0.74
3.10	1.97	0.64	2.39	0.77	1.86	0.60
3.74	3.15	0.84	2.72	0.73	1.84	0.49
5.73	2.51	0.44	3.01	0.52	1.94	0.34
4.33	4.28	0.99	3.48	0.80	1.95	0.45
AVERAGE:	3.46	1.01	3.28	1.12	2.10	0.75

K_{LC} : COMPUTED VALUE

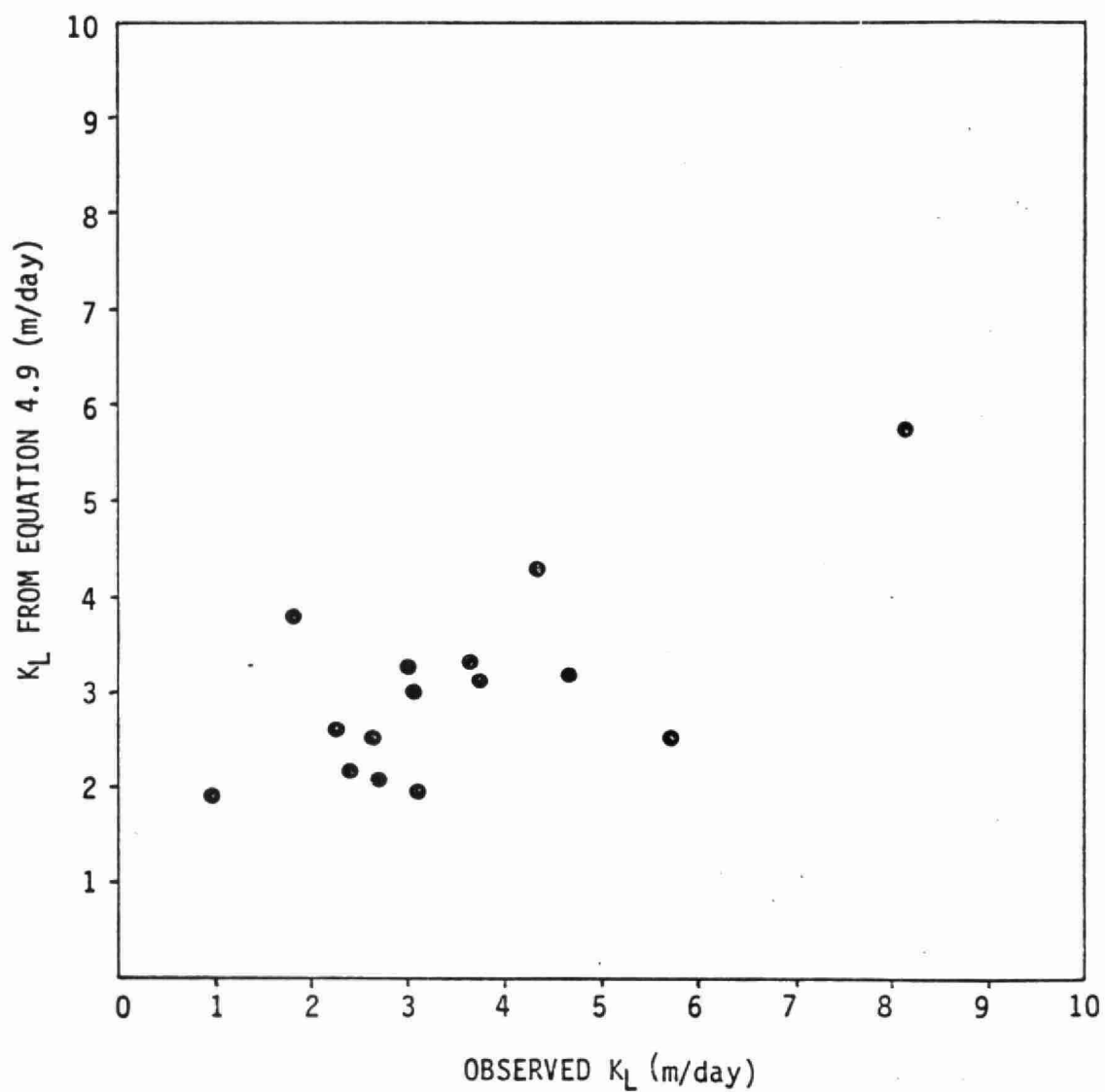


FIGURE 4.1 - COMPARISON OF K_L FROM EQUATION 4.9
WITH THE OBSERVED VALUES

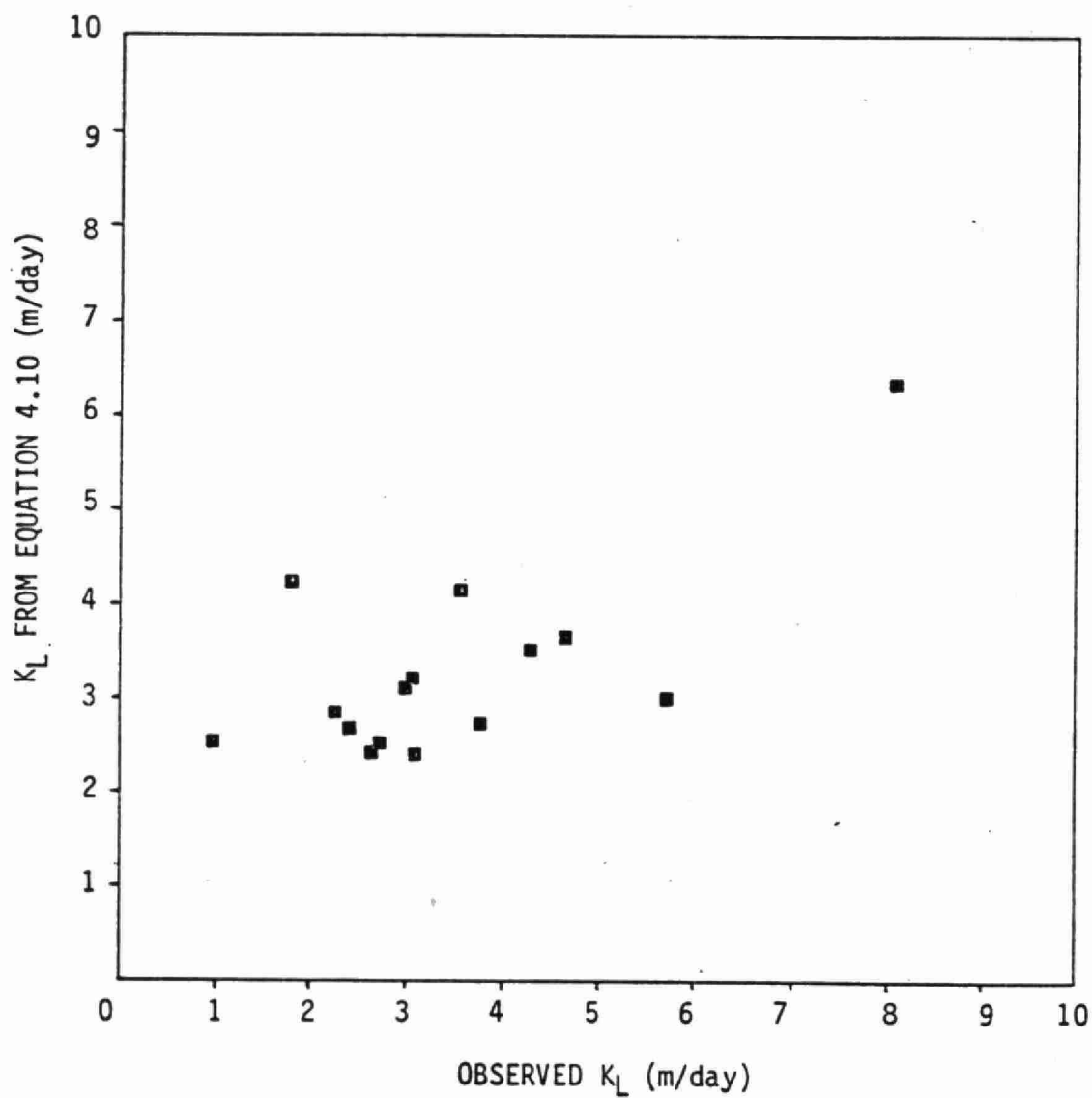


FIGURE 4.2 - COMPARISON OF K_L FROM EQUATION 4.10
WITH THE OBSERVED VALUES

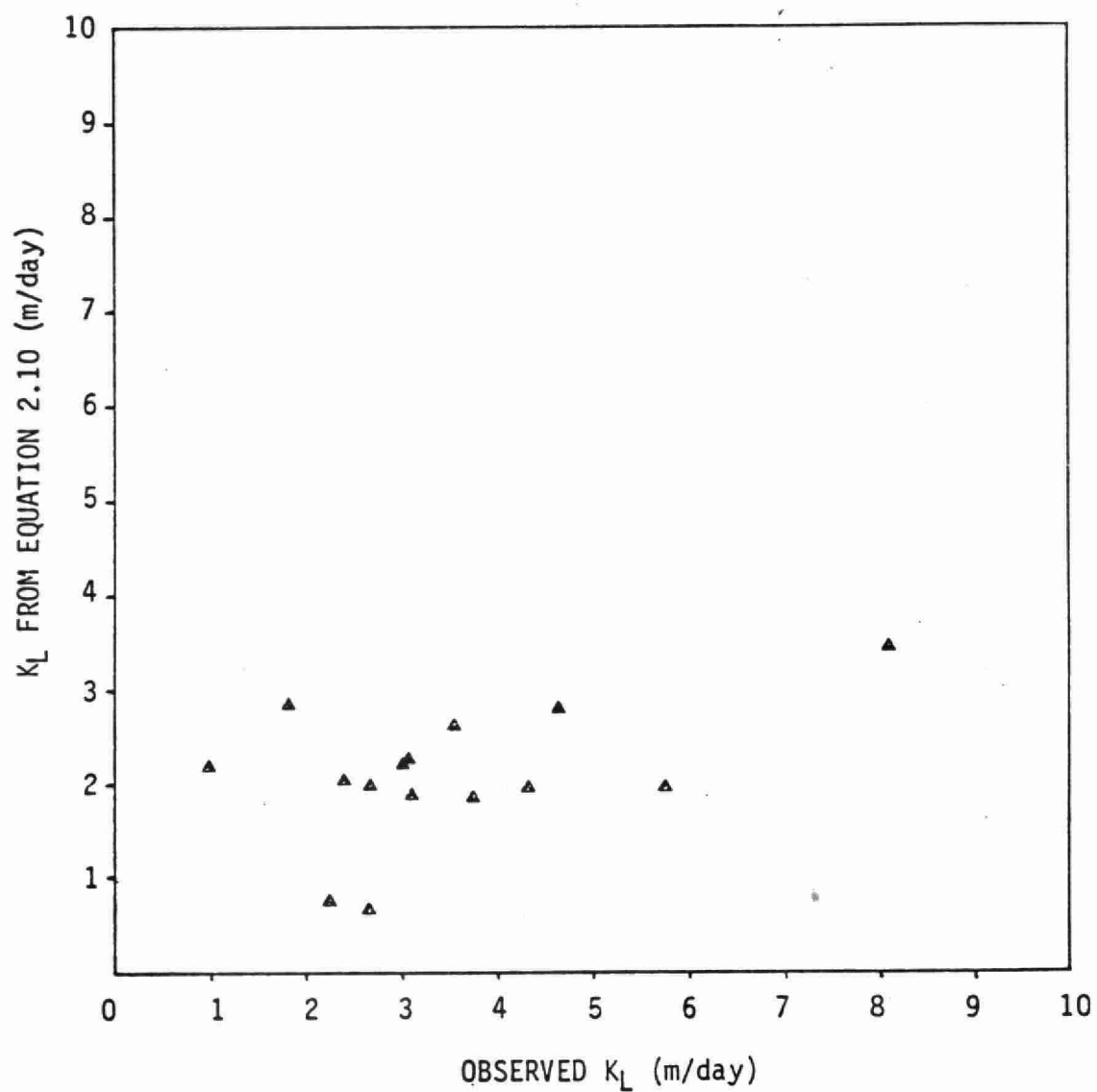


FIGURE 4.3 - COMPARISON OF K_L FROM EQUATION 2.10 OF RATHBUN AND TAI (1981) WITH THE OBSERVED VALUES

Rathbun and Tai (1981) have presented values of liquid film coefficient at 20°C (K_{LO}) applicable to the organic compounds benzene, chloroform, methylene chloride and toluene for several streams and rivers. The values of K_{LO} for these four compounds were found to be approximately the same, based on laboratory studies. These K_{LO} values are related to the K_L values for ethylene by the relationship $K_{LO} = 0.753 K_L$. The river hydraulic data given by Rathbun and Tai (1981) include water depth, velocity and discharge; but the bed slopes and reach lengths are not reported. These data were thus utilized to compute the values of liquid film coefficients for ethylene from Equation 4.10. Table 4.3 shows the hydraulic data for the streams as well as the K_L values obtained from $K_{LO} = 0.753 K_L$ (Rathbun and Tai, 1981). Herein, these calculated K_L values will be referred to as "observed" values. The range of the various parameters are as follows:

Discharge	0.027 - 93.50 m ³ /s
Water depth	0.053 - 2.330 m
Velocity	0.060 - 0.747 m/s
K_L	0.46 - 7.66 m/day

The predictions of Equation 4.10, given in Table 4.3, are seen to range from 1.87 to 10.10 m/day. The average of the "observed" and computed K_L values are 2.00 and 4.69 m/day, respectively; and the ratios between the "computed" and observed values range from 0.75 to 7.79, the average ratio being 3.53. These results show that Equation 4.10 overestimates K_L values for the streams and rivers for which data are reported by Rathbun and Tai (1981). It is recalled that Equation 2.10 developed by Rathbun and Tai (1982) underestimates K_L values for provincial streams and rivers. These discrepancies are likely to be due to the possible effects of such factors as wind velocity, bed slope, and the presence of other chemical compounds in the streamwaters. It is also possible that the indirect method of estimating the "observed" K_L values for ethylene has contributed, to some extent, for these discrepancies.

TABLE 4.3
COMPARISON OF PREDICTIONS OF EQUATION 4.10
WITH DATA OF RATHBUN AND TAI (1981)

Z (m)	U (m/s)	K _{L0} (m/day)	K _{LC} (m/day)	$\frac{K_{LC}}{K_{L0}}$
0.472	0.160	2.31	3.91	1.69
0.285	0.305	2.51	4.88	1.94
0.289	0.439	7.66	5.78	0.75
0.387	0.317	2.47	5.20	2.11
0.053	0.160	2.12	2.82	1.33
0.090	0.150	1.46	2.96	2.03
0.082	0.150	1.33	2.92	2.20
0.070	0.060	0.46	1.87	4.03
0.260	0.160	0.88	3.58	4.08
0.270	0.085	0.48	2.69	5.63
0.180	0.210	0.92	3.84	4.19
0.280	0.180	1.73	3.82	2.21
0.482	0.160	1.04	3.92	3.77
0.290	0.270	1.39	4.63	3.32
0.518	0.408	0.78	6.10	7.79
0.579	0.552	5.79	7.13	1.23
0.270	0.088	0.68	2.73	4.04
0.948	0.144	1.25	4.14	3.32
0.701	0.171	4.78	4.28	0.90
1.240	0.546	0.81	7.95	9.82
1.270	0.539	1.46	7.94	5.43
2.330	0.747	1.73	10.10	5.85
AVERAGE:		2.00	4.69	3.53

K_{L0} : "OBSERVED"; K_{LC} : COMPUTED

4.5 Sensitivity Analysis

4.5.1 General Procedure:

A knowledge of the sensitivity of various dependent parameters on the independent variables appearing in Equations 4.7 - 4.10 will aid in identifying the relative importance of the dependent parameters in estimating K_L . Herein, the sensitivity analyses will be carried out by the method of determining the relative error or relative change (described in standard text books on calculus). Equations 4.7 - 4.10 are of the general form

$$Y = a_0 X_1^{a_1} X_2^{a_2} \dots X_n^{a_n} \quad (4.11)$$

where Y is the independent variable;

X_i ($i=1,n$), are the dependent variables;

n is the number of dependent variables;

a_0 is a constant; and

a_i is the exponent of X_i ($i=1,n$)

In order to determine the relative change in Y due to a given relative change in X_1 , Equation 4.11 is differentiated with respect to X_1 to obtain

$$\frac{dY}{dX_1} = a_0 a_1 X_1^{a_1-1} X_2^{a_2} \dots X_n^{a_n} \quad (4.12)$$

From Equations 4.11 and 4.12, the following relationship is obtained:

$$\frac{dY}{Y} = a_1 \frac{dX_1}{X_1} \quad (4.13)$$

In Equation 4.13, (dX_1/X_1) and (dY/Y) denote relative changes in X_1 and Y , respectively. Thus, for a given relative change in X_1 , the relative change in Y can be obtained from Equation 4.13. In other words, the sensitivity of X_1 can be determined from this relationship. Similar analyses can be carried out for the other variables X_i ($i=2,n$) appearing in Equation 4.11.

4.5.2 Sensitivity of Various Parameters:

The general procedure described in the previous section has been applied to examine the sensitivities of various parameters of Equations 4.7 - 4.10. The results of sensitivity analyses are presented in Table 4.4. In these analyses, the relative change in the independent variable due to a relative change of 20% in the dependent variable under consideration, has been determined. The results shown in Table 4.4 are arranged in a decreasing order of relative importance of various dependent parameters. The most sensitive parameters are the molecular diffusivity of organic compound and kinematic viscosity of water.

4.6 Relation Between Liquid Film Coefficients of Tracer Gases and Organic Compounds

4.6.1 Review of Relationships:

Based on studies carried out by Rathbun, et al (1978) and Rainwater and Holley (1984), the liquid film coefficients of any two volatile compounds are related by

$$R = \frac{K_{LG}}{K_{LORG}} \quad (4.14)$$

where K_{LG} and K_{LORG} are the liquid film coefficients of a tracer gas and organic compound, respectively; and R is the ratio between the two coefficients. Rathbun, et al (1978) and Rainwater and Holley (1984) have presented values of R between various tracer gases, determined from laboratory experimental studies. Also, the value of R between ethylene gas and a group of four organic compounds, has been given by Rathbun and Tai (1981) as stated earlier (see Section 4.4).

The values of R can also be calculated by making use of molecular diameter, critical volume or molecular weight of organic compounds (see Chapter II). In a recent publication, Rainwater and Holley (1984) have presented theoretical aspects related to the use of molecular diameter and critical volume in determining the values of R . The relationship obtained by Rainwater and Holley (1984) can be written in the form

TABLE 4.4
RESULTS OF SENSITIVITY ANALYSES

Relationship	Dependent Variable		Independent Variable	
	Parameter	Relative Change (%)	Relative Change (%)	Parameter
Equation 4.7	UZ/D_m	20.0	-37.8	K_L/U
	UZ/v	20.0	37.0	
	B/Z	20.0	8.0	
	U^2/gZ	20.0	7.0	
	LS/Z	20.0	3.2	
Equation 4.8	UZ/D_m	20.0	-31.8	K_L/U
	UZ/v	20.0	30.2	
	U^2/gZ	20.0	- 4.6	
Equation 4.9	D_m	20.0	37.8	K_L
	v	20.0	-37.0	
	B	20.0	8.0	
	U	20.0	5.2	
	Z	20.0	- 5.0	
	LS	20.0	3.2	
Equation 4.10	D_m	20.0	31.8	K_L
	v	20.0	-30.2	
	U	20.0	9.2	
	Z	20.0	3.0	

$$R_V = \frac{K_{LG}}{K_{LORG}} = \left(\frac{d_{ORG}}{d_G} \right)^{0.942} = \left(\frac{V_{CORG}}{V_{CG}} \right)^{0.314} \quad (4.15)$$

where R_V is the ratio based on critical volumes; d_G and d_{ORG} denoted, in order, the molecular diameters of tracer gas and organic compound; and V_{CG} and V_{CORG} are the critical volumes of the tracer gas and organic compound, respectively. This relationship is based on the assumption that the molecules are spherical, and hence, the critical volume is proportional to the cube of the diameter. The exponent 0.942 appearing in Equation 4.15 is very close to unity, and hence, the relationship between R and the ratio of molecular diameters is a reasonable agreement with Equation 2.7 (i.e., $K_L \propto d_m^{-1}$).

Based on the relationship of K_L to molecular weight presented in Chapter II (Equation 2.6), the following expression is obtained.

$$R_M = \frac{K_{LG}}{K_{LORG}} = \left(\frac{M_{ORG}}{M_G} \right)^{0.5} \quad (4.16)$$

where R_M is the ratio based on the molecular weights, and M_G and M_{ORG} denote, in order, the molecular weights of tracer gas and organic compound. A rigorous evaluation of Equation 4.16 (similar to that for Equation 4.15) could not be found in the literature, except for the studies of Southworth (1979) described in Chapter II.

This review indicates that either one or both of the above relationships (i.e., Equations 4.15 and 4.16) can be the basis for adjusting the K_L values of tracer gases to organic compounds of interest. A comparative study of observed and computed values of R will aid in deciding the validity of Equations 4.15 and 4.16.

4.6.2 Evaluation of Relationships:

Laboratory experimental data presented by Rathbun, et al (1978), Rathbun and Tai (1981), Roberts and Dandliker (1983), Kaczmar, et al (1984) and Mackay and Yuen (1983) will be utilized to evaluate the validity of Equations 4.15 and 4.16.

Rathbun and Tai (1981) present K_L values for oxygen and four organic compounds whereas Rathbun et al (1978) report desorption - absorption rates (per day) associated with ethylene, propane and oxygen. The studies of Roberts and Dandliker (1983), and Kaczmar, et al (1984) include absorption rates of oxygen (per day) and desorption rates (termed mass transfer rate constants expressed in the units per second) for several volatile compounds. Thus, exchange rates for oxygen are measured in all of these studies. The analyses presented below involve ratios of exchange rates between oxygen and an organic compound. These ratios have been determined by using either the K_L values or the absorption and desorption rates. For the sake of convenience, the exchange rates (i.e., liquid film coefficients, and absorption and desorption rates) will be denoted by K' .

The following relationships permit computation of the ratios of exchange coefficients:

$$R_E = (K' \text{ for oxygen} / K' \text{ for ethylene}) \quad (4.17)$$

$$R_{O_2} = (K' \text{ for oxygen} / K' \text{ for organic compound}) \quad (4.18)$$

$$R_{ORG} = (R_{O_2} / R_E) = (K' \text{ for ethylene} / K' \text{ for organic compound}) \quad (4.19)$$

The ratios obtained from Equations 4.17 -4.19 will be termed the observed ratio values since they are obtained from measured K' values. Table 4.5 shows the observed R_{O_2} and R_{ORG} values for various volatile compounds including oxygen. The Henry's law constants and molecular weights of the compounds are also given in this table.

Mackay and Yuen (1983) obtained liquid film coefficients (K_L) at six wind speeds (range 5.96 - 13.2 m/s) for eleven organic compounds. The compounds tested as well as their Henry's law constants, molecular weights and critical volumes are given in Table 4.5. Since oxygen has not been included in this study, the values of R_{ORG} , defined by Equation 4.19, were calculated indirectly. First, the ratios (R_{BZ}) were computed by considering benzene as the reference compound. Then, these ratios were converted to the R_{ORG} values through the use of the observed ratio ($K' \text{ for ethylene} / K' \text{ for benzene}$) = 1.29. The relationships utilized are:

TABLE 4.5

RATIOS OF EXCHANGE COEFFICIENTS FOR VOLATILE COMPOUNDS

Source of Data	Compound	Henry's Law Constant (atm-m ³ /mol at 20°C and 1 atm)	Molecular Weight (gram/mol)	Critical Volume (cm ³ /mol)	Observed Ratio *		Computed Ratio			
					R _{O2}	R _{ORG}	Equation 4.15		Equation 4.16	
							R _{V O2}	R _{VORG}	R _{MO2}	R _{MORG}
Henry's Law Constant > 10 ⁻³ atm-m ³ /mol										
Rathbun et al (1978) ^a	Oxygen	0.73	32.0	73.4	1.00		1.00		1.00	
	Ethylene	8.6	28.1	120.0	1.15	1.00	1.17	1.00	0.943	1.00
	Propane	1.6 x 10 ⁻²	44.1	205.0	1.39	1.21	1.38	1.18	1.17	1.24
Rathbun & Tai (1981) ^b	Benzene	4.4 x 10 ⁻³	78.1	262.0	1.49	1.29	1.49	1.27	1.56	1.65
	Toluene	5.2 - 6.6 x 10 ⁻³	92.2	316.0	1.56	1.36	1.58	1.35	1.70	1.80
	Methylene chloride	3.0 x 10 ⁻³	84.9	193.0	1.45	1.26	1.35	1.15	1.63	1.73
	Chloroform	3.4 x 10 ⁻³	119.4	238.0	1.50	1.30	1.45	1.24	1.93	2.05
Roberts and Dandliker (1983) ^c	Chloroform	3.4 x 10 ⁻³	119.4	238.0	1.79	1.56	1.45	1.24	1.93	2.05
	Carbon tetrachloride	2.3 - 2.5 x 10 ⁻²	153.8	277.0	1.62	1.41	1.52	1.30	2.19	2.32
	Dichlorodifluoromethane	1.5	120.9	215.0	1.54	1.34	1.40	1.20	1.94	2.06
	Tetrachloroethene	8.3 x 10 ⁻³	165.8	308.0	1.66	1.44	1.57	1.34	2.28	2.42
	1,1,1-trichloroethane	3.6 - 18 x 10 ⁻³	133.4	283.0	1.67	1.45	1.53	1.31	2.04	2.16
	Trichloroethene	1.0 x 10 ⁻²	131.4	268.0	1.63	1.42	1.50	1.28	2.02	2.14
Kaczmar et al (1984) ^d	Chloroform	3.4 x 10 ⁻³	119.4	238.0	1.59	1.38	1.45	1.24	1.93	2.05
	Bromodichloromethane	1.3 x 10 ⁻³	163.8	259.0	1.82	1.58	1.49	1.27	2.26	2.40
Mackay and Yuen (1983) ^e	Benzene	4.4 x 10 ⁻³	78.1	262.0		1.29		1.49		1.67
	Toluene	5.2 - 6.6 x 10 ⁻³	92.2	316.0		1.25		1.58		1.80
	1,2-dichloropropane	2.1 x 10 ⁻³	113.0	299.0		1.33		1.33		2.00
	Chlorobenzene	2.6 x 10 ⁻³	112.6	310.0		1.22		1.35		2.00
	Carbon tetrachloride	2.3 - 2.5 x 10 ⁻²	153.8	277.0		1.24		1.30		1.75
Henry's Law Constant < 10 ⁻³ atm-m ³ /mol										
Kaczmar et al (1984) ^d	Chlorodibromomethane	8.1 x 10 ⁻⁴	208.3	280.0	2.38	2.07	1.52	1.30	2.55	2.70
	Bromoform	5.8 x 10 ⁻⁴	252.8	301.0	3.45	3.00	1.56	1.33	2.81	2.98
Mackay and Yuen (1983) ^f	1,2-dibromomethane	6.3 x 10 ⁻⁴	173.9	290.0		1.56		1.32		2.49
	2-pentanone	3.2 x 10 ⁻⁵	86.1	320.0		3.26		1.36		1.75
	2-heptanone	9.0 x 10 ⁻⁵	114.2	430.0		2.77		1.49		2.02
	1-pentanol	1.0 x 10 ⁻⁵	88.2	333.0		12.40		1.38		1.77
	2-methyl-1-propanol	1.0 x 10 ⁻⁵	74.1	274.0		14.40		1.30		1.62
	1-butanol	5.6 x 10 ⁻⁶	74.1	278.0		21.52		1.30		1.62

* Average of the number of tests stated below:

^a - 81 tests for ethylene and 34 tests for propane^b - 10 tests for each of the four compounds^c - 16 tests for each of the six compounds^d - 13 tests for chloroform and 2 tests for each of the other three compounds^e - 6 tests for benzene and toluene, 4 tests for the next three compounds^f - 4 tests for the first three and 3 tests for the last three compounds

$$R_{BZ} = (K_L \text{ for benzene} / K_L \text{ for organic compound}) \quad (4.20)$$

$$R_{ORG} = 1.29 R_{BZ} \quad (4.21)$$

The values of R_{BZ} utilized herein are the average values of the ratios obtained for each of the windspeeds. Benzene and toluene were included in all the six windspeed experiments, whereas the remaining compounds were monitored at three or four windspeeds. The observed ratios (R_{ORG}), obtained from Equations 4.20 and 4.21, are presented in Table 4.5.

Four of the compounds listed in Table 4.5, namely benzene, toluene, chloroform and carbon tetrachloride, were utilized in two or more studies. The observed values of R_{ORG} for each compound, obtained from these studies, are seen to differ somewhat. This indicates the possible effects of testing conditions on the observed R_{ORG} values.

The critical volumes (V_C) for various volatile compounds were determined as outlined in Chapter V (see Section 5.5). The compounds are listed in Table 4.5 along with the corresponding values of (V_C) and molecular weights (M). These data have been utilized to calculate the values of R and R_M according to Equations 4.15 and 4.16, respectively. The computed values of R_V and R_M for various compounds are given in Table 4.5.

The range of various parameters for the volatile compounds presented in Table 4.5 are as follows:

Molecular weight:	28.1 - 252.8 grams/mol
Critical volume:	73.4 - 316.0 cm ³ /mol
Observed ratio (R_{O2}) between oxygen and: organic compound	1.00 - 3.45
Ratio (R_{ORG}) between ethylene and organic: compound, based on observations	1.00 - 21.52
Ratio (R_{V02}), computed from critical: volumes using Equation 4.15	1.00 - 1.58
Ratio (R_{VORG}), based on critical volumes:	1.00 - 1.35
Ratio (R_{M02}), computed from molecular: weights using Equation 4.16	0.943 - 2.81

Ratio (R_{MORG}), based on molecular weights: 1.00 - 2.98

A comparison of the computed R_V and R_M values with the corresponding observed ratios for various compounds indicates that:

- (1) the computed values of R_V , obtained from Equation 4.15 using the critical volumes, are in reasonable agreement with the corresponding observed ratios with the exception of the compounds for which the Henry's law constants are smaller than 10^{-3} atm-m³/mol.
- (2) the computed values of R_M , obtained from Equation 4.16 using the molecular weights, differ from the corresponding observed ratios for about 50% of the compounds listed in Table 4.5; however, for bromoform, the computed R_M value is in agreement with the observed ratio.
- (3) the observed R values for chloroform are in the range 1.30 - 1.56, indicating possible effects of variations in the testing conditions.

This analysis suggests that Equation 4.15 can be utilized to compute the values of R required for adjusting K_L values of highly volatile compounds (Henry's law constant $>10^{-3}$ atm-m³/mol), although some limitations are evident. It is recommended to evaluate the validity of Equations 4.15 and 4.16 for a broader range of organic compounds as data become available, as well to undertake investigations for developing similar relationships for compounds of moderate and low volatility.

4.7 Computation of Liquid Film Coefficient of an Organic Compound

The various steps involved in computing the liquid film coefficient for a given organic compound are outlined below. The computational procedure is then illustrated by an example.

Computational Procedure:

1. For the given organic compound, obtain the Henry's law constant (see Chapter V). This computational procedure is generally valid for compounds having Henry's constants greater than 10^{-3} atm - m³/mol.
2. Obtain hydraulic data for the desired reaches (or segments) of a given river channel. These data include: discharge, reach length, width, depth, velocity and bed slope. (Note: If the latter is unknown, Equation 4.10 could be utilized.)
3. For the desired river water temperature, obtain the values of density and absolute viscosity, which are readily available in standard fluid mechanics text books or handbooks on physical and chemical properties (eg. Weast and Astle, 1979).
4. Determine the molar volume (V_B) for ethylene gas by the LeBas method as outlined in Section 5.5.
5. Calculate D_m for ethylene gas by using the Hayduk-Laudie relationship (Equation 3.4).
6. Compute the liquid film coefficient (K_{LE}) for ethylene gas from Equation 4.9 or 4.10 (depending on whether the bed slope is known or unknown).
7. Calculate the critical volume (cm³/mol) for the organic compound as outlined in Section 5.5 (see Chapter V).
8. Determine the ratio (R_v) required for calculating K_{LORG} from K_{LE} , using Equation 4.15. (Note: Critical volume for ethylene gas = 120 cm³/mol.)
9. Calculate K_{LORG} for the organic compound from

$$K_{LORG} = K_{LE}/R_v$$

Example: The hydraulic data for the Speed River, survey date 8/24/78, reach BD, given in Table 3.1, have been considered in this illustrative example. The organic compound selected is methylene chloride (CH_2Cl_2). The computations as per the above step-by-step procedure are as follows:

1. For methylene chloride, Henry's law constant = 3×10^{-3} atm-m³/mol (see Appendix).
2. The hydraulic data for the reach BD of the Speed River are as follows:

$$Q = 2.43 \text{ m}^3/\text{s}; L = 2380 \text{ m}; S = 0.0011; B = 38.6 \text{ m}; \\ Z = 0.414 \text{ m}; U = 13,392.0 \text{ m/day}; LS = (2380)(0.0011) = 2.618 \text{ m}$$

3. River water temperature = 19.0°C

$$\rho = 998.4052 \text{ kg/m}^3; \mu = 88.73 \text{ kg/m-day} = 1.027 \text{ centipoise} \\ \nu = \mu/\rho = 0.0889 \text{ m}^2/\text{day}$$

4. The Molar volume (V_B) of ethylene gas (C_2H_4) by the LeBas method (see Table 5.5 for incremental volumes) is:

$$V_B = \frac{2(14.8)}{2(\text{C})} + \frac{4(3.7)}{4(\text{H})} = 44.4 \text{ cm}^3/\text{mol}$$

5. From Equation 3.4,

$$D_m = \frac{13.26 \times 10^{-5}}{(1.027)^{1.14} (44.4)^{0.589}} = 1.3773 \times 10^{-5} \text{ cm}^2/\text{s} \\ = (1.3773 \times 10^{-5}) (\text{cm}^2/\text{s}) (86400) (\text{s/day}) / (10^4) (\text{cm}^2/\text{m}^2) \\ = 1.19 \times 10^{-4} \text{ m}^2/\text{day}$$

6. From Equation 4.9,

$$K_{LE} = \left[\frac{(2.7) (7.3206 \times 10^{10})^{0.35} (0.0889)^{-1.85} (1.19 \times 10^{-4})^{1.89}}{(38.6)^{0.44} (0.414)^{-0.25} (13392)^{0.25} (2.618)^{0.16}} \right] \\ = 4.28 \text{ m/day}$$

7. The critical volume of methylene chloride (CH_2Cl_2), calculated by Lydersen's method outlined in Section 5.5, is as follows:

$$V_C = 40 + 55 + 2(49) = 193 \text{ cm}^3/\text{mol} \\ - \frac{1}{\text{CH}_2} - 2[-\text{Cl}]$$

The critical volume of ethylene gas is 120 cm³/mol.

8. From Equation 4.15,

$$R_V = (193/120)^{0.314} = 1.16$$

9. The liquid film coefficient of methylene chloride is

$$K_{L_{\text{ORG}}} = (4.28/1.16) = 3.69 \text{ m/day}$$

V CHEMICAL STRUCTURE AND VOLATILIZATION

5.1 Relationship Between Henry's Law Constant and Volatilization

The ability of an organic compound to volatilize from water is governed by two specific parameters; the vapour pressure (P_V) of the compound and the solubility of the compound (C_S). These are related as shown in Equation 5.1 to give the compound specific Henry's law constant (H), which is used as

$$H = P_V/C_S \quad (5.1)$$

a measure of the chemical's ability to volatilize from water. P_V is usually given with units of atm and C_S in mol/m³ which results in the Henry's law constant (H) having units of atm m³/mol. When H is calculated using Equation 5.1 P_V and C_S used should be for the same temperature and physical state of the chemical and the data should be for the pure state. The relationship of Henry's law constant to the transfer resistance in the liquid film was reviewed in Chapter II. In general, a compound with a Henry's law constant of less than 10⁻⁷ atm m³/mol is regarded as nonvolatile, from 10⁻³ to 10⁻⁷ as moderately volatile and greater than 10⁻³ as volatile.

Since Henry's constants are not readily available in tabulated form, they are usually calculated from data on vapour pressures (P_V) and solubilities. Vapour pressure and solubility data can often be found in literature sources such as Weast (1980-81), Perry and Chilton (1963), Dean (1979), Sax (1979), and Verschueren (1977). If vapour pressure and solubility data are not readily available, they can be estimated from the basic properties of the compound of concern, as outlined in the following sections.

5.2 Estimation of Vapour Pressures

The vapour pressures for organic compounds under environmental conditions can be estimated from the normal boiling points or from the structure alone if boiling point data are not available.

Estimation of Vapour Pressure When Boiling Point Data are Available:

Two methods of estimating vapour pressures applicable to environmental needs have been described in detail by Grain in Lyman et al (1982). These are based on the correlation equation of Antoine and of Watson. Both of these are derived from integration of the Clausius-Clapeyron equation shown below:

$$\frac{d(\ln P_v)}{dt} = \frac{\Delta H_v}{\Delta Z R T^2} \quad (5.2)$$

where ΔH_v is the heat of vaporization for the compound; ΔZ , R are defined below; and T is the temperature in degrees Kelvin.

Vapour Pressure from the Equation of Antoine:

The procedure based on the Antoine relationship is only applicable to compounds that are in the liquid or vapour phase at the temperature of interest. The equation relating vapour pressure (P_v) and the normal boiling point (T_b ; at one standard atmosphere pressure) is:

$$\ln P_v = \frac{\Delta H_{vb} (T_b - C_2)^2}{\Delta Z R T_b^2} \left[\frac{1}{(T_b - C_2)} - \frac{1}{(T - C_2)} \right] \quad (5.3)$$

where ΔZ is the dimensionless compressibility factor for the gas at the normal boiling point and is assumed to be equal to 0.97;

ΔH_{vb} is the heat of vaporization at the normal boiling point with units of cal/mol which can be evaluated using the equation

$$\Delta H_{vb} = K_F (8.75 + R \ln T_b) \quad (5.4)$$

the gas constant R is equal to 1.987 cal/deg mol and K_F is a constant based on the dipole moment of the compound. K_F factors are available from a number of sources (Fishtine 1963; Lyman et al, 1982). Typical ranges for some classes of organic

compounds are:

1. Hydrocarbons: 0.97 - 1.01
2. Halocarbons (fluoro, chloro, bromo and iodo): 1.00 - 1.05
3. Carbonyl compounds (esters, ketones and aldehydes):
1.01 - 1.14
4. Nitrogen compounds (amines, nitriles and nitros): 1.01 - 1.16
5. Thiols and Sulfides: 1.01 - 1.05
6. Monofunctional alcohols: 1.20 - 1.31
7. Polyfunctional alcohols (glycols, etc.): 1.33 - 1.38
8. Ethers: 1.01 - 1.08

When a value for K_F is not available, a default value of 1.06 is used. C_2 is a constant whose value can be estimated from (Thomson, 1959),

$$C_2 = 18 + 0.19 T_b \quad (5.5)$$

Vapour Pressure from the Modified Watson Correlation:

During the integration of the Clausius-Clapeyron Equation (5.2) if the ratio $\Delta H_v/\Delta Z$ is not assumed to be constant with varying temperatures but is expressed as a function of temperature, the resulting expression should be more exact. Grain in Lyman et al (1982) reports that Equation 5.6, a modification of the Watson correlation, is satisfactory with $T_{pb} = T/T_b$.

$$\Delta H_v \approx \Delta H_{vb} (3 - 2 T_{pb})^m \quad (5.6)$$

and m is a constant (see below). Equation 5.6 is substituted into Equation 5.2 which is then integrated by parts. Grain states that sufficient accuracy is obtained even when only the first term is used. Thus, the equation relating P_v with ΔH_{vb} becomes:

$$\ln P_v = \frac{\Delta H_{vb}}{\Delta Z R T_b} \left\{ 1 - \frac{(3-2T_{pb})^m}{T_{pb}} - 2m (3 - 2T_{pb})^{m-1} \ln T_{pb} \right\} \quad (5.7)$$

The following values for the constant m are chosen on the basis of the physical state of the compound at the environmental temperature:

1. liquids $m = 0.19$
2. solids - if $T_{pb} > 0.6$, $m = 0.36$
 - if $0.6 > T_{pb} > 0.5$, $m = 0.8$
 - if $T_{pb} < 0.5$, $m = 1.19$

R is equal to 1.987 cal/deg mol, $\Delta H_{vb}/T_b$ is calculated using Equation 5.3 and $\Delta Z = 0.97$.

The value of P_v obtained by this method has units of atmospheres.

Vapour Pressure from Boiling Points Obtained at Reduced Pressures:

For many organic compounds the boiling points have been obtained at reduced pressures for experimental convenience or to avoid decomposition of the compound. As a result, adaptations of Equations 5.3 and 5.5 are needed to allow the estimation of P_v for these compounds.

Grain has approximated the ratio of the heat of vapourization to temperature as

$$\frac{\Delta H_{v1}}{T_1} = K_F [8.75 + R(\ln T_1 - \ln P_1)] \quad (5.8)$$

When Equation 5.8 is used, the expression for vapour pressure based on Antoine's equation becomes

$$\ln P_v = \ln P_1 + \frac{\Delta H_{v1} (T_1 - C_2)^2}{Z_b R T_1^2} \left[\frac{1}{(T_1 - C_2)} - \frac{1}{(T - C_2)} \right] \quad (5.9)$$

The expression for vapour pressure, based on the modified Watson correlation, becomes

$$\ln P_v = \ln P_1 + \frac{\Delta H_{v1}}{\Delta Z R T_1} \left\{ 1 - [3 - 2 (T/T_1)]^m \left(\frac{T_1}{T} \right)^{-2m} [3 - 2 (T/T_1)]^{m-1} \ln(T/T_1) \right\} \quad (5.10)$$

Note that Equation 5.9 is only valid for liquids while Equation 5.10 is valid for liquids and solids.

Estimation of Normal Boiling Point from Chemical Structure:

The normal boiling point of a compound is defined as the boiling point at one standard atmosphere. Boiling point data are usually available in the literature. However, for those compounds where data is not readily available, an estimation procedure is necessary.

Most methods for the estimation of boiling point are based on correlations of parameters that are affected by chemical structure with known boiling points. Usually, the correlations are developed using relatively simple compounds containing one functional group. Chlorobenzene is considered to have one functional group, the chlorine substituent on the benzene ring. It is usually assumed that multifunctional compounds can be treated by simply adding up the effect of the various functional groups. For example, the boiling point of dichlorobenzene which has two chlorine functional groups would be estimated by doubling the effect of having only one chlorine functional group as is the case with chlorobenzene.

The estimation procedure described herein is that of Meissner (1949). The method is based on the correlation of boiling point with chemical type. The equation for the boiling point in degrees Kelvin (K) is:

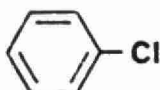
$$T_b = \frac{637 [R_D]^{1.47} + B}{[P]} \quad (5.11)$$

R_D is the molar refraction and can be estimated using the atomic refraction contribution method (see below). P is the parachor of the compound which may be regarded as the molecular volume of a liquid having a surface tension of unity (Quayle, 1953). It can be estimated by an updated version of Sugden's method (Mumford and Phillips; 1928, 1929). B is a constant whose value depends on the class of the compound.

Estimation of R_D and P :

R_D and P are estimated by adding the contributions appropriate for each atom, bond type, or structural unit. The contributions for each structural feature are given a number of literature sources (Perry and Chilton, 1963; Lyman et al 1982). The method is best described using chlorobenzene as an example.

Chlorobenzene (C_6H_5Cl) has the structure:



The molar refraction (R_D) is estimated as:

$$\begin{aligned} R_D &= 6 \text{ (contribution for a carbon atom)} \\ &\quad +5 \text{ (contribution for a hydrogen atom)} \\ &\quad +3 \text{ (contribution for a double bond)} \\ &\quad +1 \text{ (contribution for a chlorine atom)} \end{aligned}$$

$$\begin{aligned} \text{thus } R_D &= 6 \text{ (2.418)} \\ &\quad +5 \text{ (1.100)} \\ &\quad +3 \text{ (1.733)} \\ &\quad +1 \text{ (5.967)} \\ R_D &= 31.174 \end{aligned}$$

R_D could be more efficiently calculated by adding the contribution for a phenyl group (C_6H_5) to the contribution for a chlorine atom (Cl). Thus

$$\begin{aligned} R_D &= 1 \text{ (contribution for a phenyl group)} \\ &\quad +1 \text{ (contribution for a chlorine)} \end{aligned}$$

$$\begin{aligned} R_D &= 25.207 \\ &\quad + 5.967 \\ R_D &= 31.174 \end{aligned}$$

For the parachor (P) the same techniques can be used, eg:

$$\begin{array}{r} P = 6 (9.2) \\ +5 (15.4) \\ +3 (19.0) \\ +1 (55.0) \\ \hline P = 244.2 \end{array}$$

or, by using the contribution for a phenyl group,

$$\begin{array}{r} P = 1 (190.0) \\ + (55.0) \\ \hline P = 245.0 \end{array}$$

Note that in the calculation of P using a value of 190 for the phenyl group a slightly different value of P is obtained. This slight variation is acceptable within the expected error of the method (see below). For B, the Literature (Perry and Chilton, 1973; Lyman et al, 1982) gives a value of -2500 for aromatic hydrocarbons. This value of B has been chosen as there is no value for B for chlorinated aromatic hydrocarbons. To calculate a value of T_b , one substitutes the values of R_D , P and B into Equation 5.11 to obtain

$$T_b = 398 \text{ K} = 125 \text{ C}$$

As a comparison, Weast and Astle (1980-81) reports value of the normal boiling point for chlorobenzene as 132°C. The calculated value of 125°C is within 5% of the reported value. Generally, this method has an average error of 2% with a maximum error of about 8%.

5.3 Estimation of the Aqueous Solubility of a Compound

As indicated by Equation 5.1, Henry's law constant is inversely proportional to the aqueous solubility. Solubilities of organic compounds vary over a wide range with most organic compounds having solubilities from 1 to 100,000 µg/L although some organics have solubilities as low as 0.001 µg/L while others are infinitely

soluble in water. Due to this extremely wide range of solubilities the value of the Henry's constant - which governs the volatilization rate - is highly dependent on the solubility.

Literature values for the solubility of organic compounds are usually readily available. However, a method of estimating the solubility of organics in water is needed for compounds for which data are not obtainable or for which none has been determined.

Solubility From Octanol-Water Partition Coefficients:

A number of correlation relationships between the octanol-water partition coefficient (K_{ow}) and the aqueous solubility (C_s) have been presented in a recent publication Lyman et al, (1982). Table 5.1 presents a selected number of these correlations. An example of the use of one of these correlation equations will be presented during the discussion of the octanol-water partition coefficient.

Octanol-Water Partition Coefficient from Chemical Structure:

Lyman et al (1982) present a review of the available methods for the estimation of K_{ow} . The methods include those based on fragment constants which are summed to give the octanol-water partition coefficient, methods based on the estimation of activity coefficients, by calculation of free energies of solvation, via topological indices, and by linear regressions on to other physical-chemical parameters. The method which best meets the criterion of accuracy, ease of calculation, and applicability to a wide range of compounds is that of Hansch and Leo (1979). This method makes use of fragment constants (f) and structural factors (F) to estimate K_{ow} . Values of f and F can be found in a number of sources (Hansch and Leo, 1979; Lyman et al, 1982). In addition, Hansch and Leo (1979) provide a listing of K_{ow} values for thousands of compounds.

Calculations of the octanol-water partition coefficient are carried out in terms of $\log K_{ow}$ using the equation

$$\log K_{ow} = \text{sum of fragments } (f) + \text{factors } (F) \quad (5.12)$$

Table 5.1

EQUATIONS RELATING AQUEOUS SOLUBILITY
TO OCTANOL-WATER PARTITION COEFFICIENT

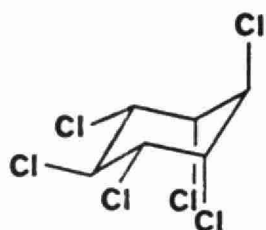
<u>Equation</u>	<u>Ref</u>	<u>Units of Solubility (s)</u>	<u>Classes of Compounds</u>
$\log S = -1.12 \log K_{OW} + 7.30 - 0.015 t_m^{\dagger}$	a	umol/L	All types; especially aromatics and chlorinated hydrocarbons
$\log 1/S = 1.339 \log K_{OW} - 0.978$	b	mol/L	Alcohols, Ketones, Esters, Ethers, Alkyl halids, Alkynes, althenes, Aromatics, Alkanles
51 $\log S = -2.38 \log K_{OW} + 12.90$	b	umol/L	Phosphate esters
$\log S = -0.9874 \log K_{OW} - 0.0095 t_m + 0.7178$	b	umol/L	Halogenated benzene compounds
$\log S = -0.88 \log K_{OW} - 0.01 t_m - 0.012$	b	mol/L	Polycyclic Aromatic Hydrocarbons
$\log S = -0.962 \log K_{OW} + 6.50$	b	7 u mol/L	Halogenated organics containing 1 or 2 carbons only

a: Banarjete et al (1980)

b: Lyman et al (1982) and references cited

†: t_m is the melting point of the compound. If t_m is <25°C, a default value of 25°C is used.

Although a complete description of the method is beyond the scope of this report, an example is provided in order to illustrate the method. The following example is taken from Hansch and Leo (1979). The structure of lindane ($C_6H_6Cl_6$) is:



The fragments (f) necessary for calculation of K_{OW} are:

- 6 (0.20 for each carbon);
- 6 (0.23 for each hydrogen);
- and 6 (0.06 for each chlorine)

The Factors (F) necessary for the calculation of K_{OW} are:

- (6-1) (-0.09 for bonds in a ring);
- and (6-1) (0.28 for vicinal chlorines).

By substituting these values in Equation 5.12, the calculated value of $\log K_{OW}$ for lindane is 3.89. The observed value reported by Hansch and Leo (1979) was 3.72. When the calculated $\log K_{OW}$ is substituted into the first equation of Table 5.1, an aqueous solubility of 0.018 mol/m^3 is obtained. This compares reasonably well with the value of 0.034 mol/m^3 reported by Verschueren (1977).

5.4 Henry's Constants for Compounds of Concern in Ontario

The available data for the compounds of concern to the Ministry are listed in appendix. In this appendix, the compounds have been divided into three groups:

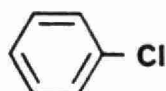
- High volatility: $H > 10^{-3} \text{ atm m}^3/\text{mol}$;
- Moderate volatility: $10^{-3} \text{ atm m}^3/\text{mol} > H > 10^{-7} \text{ atm m}^3/\text{mol}$; and
- Low volatility: $H < 10^{-7} \text{ atm m}^3/\text{mol}$.

The values of the Henry's law constant which were used to make the classification are literature values from the references cited or estimated using literature data on boiling points, vapour pressures, solubilities, etc. Where data was unavailable, an estimation of the Henry's law constant was made using the techniques of the preceding sections of this chapter. Within each group, the compounds are classified into chemical families.

5.5 Estimation of Molar and Critical Volumes

5.5.1 Molar Volume from Chemical Structure:

The molar volume (V_B) can be calculated from a knowledge of structure alone, by the LeBas method. The method has been described in texts such as Perry and Chilton (1973), Reid et al, 1977 and Lyman et al (1982). In the LeBas method, V_B is calculated by summing the additive volume increments shown in Table 5.2 for each atom and structural feature in the molecule. The procedure is best described using chlorobenzene (C_6H_5Cl) as an example. The structure of chlorobenzene is



From an examination of this structure the LeBas molar volume is estimated in the following manner:

$$\begin{aligned} V_B = & 1 \text{ (increment for chlorine)} \\ & + 6 \text{ (increment for carbon)} \\ & + 5 \text{ (increment for hydrogen)} \\ & + 1 \text{ (increment for 6-membered ring)} \end{aligned}$$

and

$$\begin{aligned} V_B = & 24.6 \\ & + 6 \quad (14.8) \\ & + 5 \quad (3.7) \\ & + 1 \quad (-15.0) \\ V_B = & 116.9 \text{ cm}^3/\text{mol} \end{aligned}$$

5.5.2 Critical Volume from Chemical Structure:

Critical volume is defined as the volume of a mole of a compound at the highest temperature that the compound can exist as a liquid. Lydersen has developed a method of calculating the critical volume (V_C) from only a knowledge of the structure of the compound. Lydersen's method has been presented in texts such as Reid, et al (1977) and Lyman et al (1982). The method is based on the summation of volume increments for each of the structural features of the organic compound. A listing of the structural features and the associated volume increments (ΔV) is given in Table 5.3. The equation for V_C is

$$V_C = 40 + \sum \Delta V$$

where the critical volume has the units of cm^3/mol . The procedure for calculating V_C is best described using an example, specifically chlorobenzene, which has the structure shown in section 5.5.1.

From an examination of the structure in conjunction with the data given in Table 5.3,

$$\begin{aligned} V_C &= 40 \\ &+ \Delta V (\text{chlorine}) \\ &+ 5 \Delta V (\text{HC= in a ring}) \\ &+ \Delta V (\text{C= in a ring}) \end{aligned}$$

$$\begin{aligned} V_C &= 40 \\ &49 \\ &5(37) \\ &+ 36 \\ V_C &= 310 \text{ cm}^3/\text{mol} \end{aligned}$$

Table 5.2

ADDITIVE VOLUME INCREMENTS FOR CALCULATING
THE LEBAS MOLAR VOLUME

Atom	Increment (cm ³ /mol)	Atom	Increment (cm ³ /mol)
C	14.8	Br	27.0
H	3.7	Cl	24.6
O (except as noted below)	7.4	F	8.7
In methyl esters and ethers	9.1	I	37.0
In ethyl esters and ethers	9.9	S	25.6
In higher esters and ethers	11.0	Ring	
In acids	12.0	3-Membered	- 6.0
Joined to S, P, N	8.3	4-Membered	- 8.5
N		5-Membered	-11.5
Double bonded	15.6	6-Membered	-15.0
In primary amines	10.5	Naphthalene	-30.0
In secondary amines	12.0	Anthracene	-47.5

Source: Reid, et al (1977)

Table 5.3

LYDERSEN'S INCREMENTS FOR CALCULATING CRITICAL VOLUMES^{a,b,c}

Increment	ΔV	Increment	ΔV
Nonring increments		Halogen increments	
$-\text{CH}_3$	55	$-\text{F}$	18
$-\text{CH}_2$	55	$-\text{Cl}$	49
$-\text{CH}$	51	$-\text{Br}$	(70)
$-\text{C}-$	41	$-\text{I}$	95
$=\text{CH}_2$	45	Oxygen increments	
$=\text{CH}$	45	$-\text{OH}$ (alcohols)	(18)
$=\text{C}-$	36	$-\text{OH}$ (phenols)	(3)
$=\text{C}=\text{C}$	36	$-\text{O}-$ (nonring)	20
$\equiv\text{CH}$	(36) ^c	$-\text{O}-$ (ring)	(8)
$\equiv\text{C}-$	(36)	$-\text{C}=\text{O}$ (nonring)	60
Ring increments		$-\text{C}=\text{O}$ (ring)	(50)
$-\text{CH}_2-$	44.5	$\text{HC}=\text{O}$ (aldehyde)	73
$-\text{CH}$	46	$-\text{COOH}$ (acid)	80
C	(31)	$-\text{COO}-$ (ester)	80
$=\text{CH}$	37	$=\text{O}$ (exc. for above combinations)	11
$=\text{C}-$	36	Nitrogen increments	
$=\text{C}=\text{C}$	36	$-\text{NH}_2$	28
Sulfur increments		$-\text{NH}$ (nonring)	(37)
$-\text{SH}$	55	$-\text{NH}$ (ring)	(27)
$-\text{S}-$ (nonring)	55	$-\text{N}-$ (nonring)	(42)
$-\text{S}-$ (ring)	(45)	$-\text{N}-$ (ring)	(32)
$=\text{S}$	(47)	$-\text{CN}$	(80)
		$-\text{NO}_2$	(78)

a. There are no increments for hydrogen.

b. All bonds shown as free are connected to atoms other than H.

c. Values in parentheses are based upon too few experimental values to be reliable.

Source: Reid, et al (1977).

VI CONCLUSIONS AND RECOMMENDATIONS

Volatilization of organic compounds in streams and rivers has been investigated through an analysis of data on ethylene and dye tracer and development of predictive relationships. The factors affecting volatilization, and conceptual models of transport at the air-water interface have been presented. The relationship of liquid film coefficients to bulk flow channel parameters and characteristic properties of organic compounds, reported in the literature, have been reviewed. The liquid film coefficients of ethylene for provincial streams and rivers have been determined by making use of data on ethylene and rhodamine WT dye tracers which were collected in the provincial streams and rivers. The development of generalized relationships among the liquid film coefficients and bulk flow channel characteristics has been accomplished through statistical and dimensional analysis techniques.

The predictive capabilities of the relationships have been evaluated by a comparative study of the observed and the predicted values of K_L for ethylene gas applicable to the provincial streams as well as other streams for which data are reported in the literature (Rathbun and Tai, 1981; 1982). A sensitivity analysis of various parameters appearing in the relationships has been presented.

The relation of liquid film coefficient (K_L) of an organic compound to the molecular weight as well as critical volume (or molecular diameter) of the compound have been evaluated with the aid of laboratory experimental data reported in the literature. From this evaluation, relationships for computing K_L values of organic compounds from the K_L values for ethylene gas, have been presented.

The computation of liquid film coefficient of an organic compound using the relationships developed herein is outlined in a step-by-step procedure, and illustrated by an example.

The relation between chemical structure and volatilization has been assessed for a number of organic compounds of concern in the province. The compounds have been grouped into a number of classes which are expected to behave similarly in streams and rivers with respect to volatilization based on the Henry's law constants. Methods of computing Henry's law constants, molar volumes and critical volumes of organic compounds have been outlined.

The major conclusions of this investigation are as follows:

1. The liquid film coefficients of ethylene in the provincial streams and rivers considered in this study are in the range 0.07 to 8.07 m/day at the observed average temperatures (or 1.07 - 7.69 m/day at 20°C).
2. The predictive abilities of the relationships among liquid film coefficient and bulk flow characteristics derived from dimensional analysis procedures are better than the statistical correlation relationships.
3. The relation obtained by Rathbun and Tai (1982) underestimates the liquid film coefficients of ethylene at 20°C for the provincial streams and rivers.
4. Application of Equation 4.10 developed herein from dimensional analysis procedure to other streams in the literature (Rathbun and Tai, 1981) results in an overestimation of the liquid film coefficients for ethylene at 20°C. However, the coefficients were indirectly calculated (but not directly measured).
5. Equations 4.9 and 4.10 can be utilized to estimate liquid film coefficients for ethylene gas in provincial streams and rivers. These relationships do not include wind velocity and hence, the computed values may involve approximations. These limitations should be given due consideration in the interpretation and application of the results.
6. The ratios (K_L for ethylene gas/ K_L for organic compound) obtained from experimental data are in reasonable agreement with the values computed by using the critical volumes of the compounds (Equation 4.15) but differed from those obtained by using molecular weights (Equation 4.16) for organic compounds having Henry's law constants $> 10^{-3}$ atm - m³/mol. Thus, the ratios obtained from Equation 4.15 are applicable to calculate K_L values of highly volatile organic compounds from those of ethylene gas.

As outlined above, an evaluation of the predictive capabilities of the relationships among K_L , bulk flow channel parameters and properties of chemical compounds indicates that the relationships may not be universally applicable to streams and rivers of differing hydraulic and water quality characteristics, as well as for different organic chemicals of public health concern. In general, there is a deficiency in the data required for development and validation of generalized relationships among K_L , channel hydraulic parameters and properties of chemicals. The effect of wind velocity is not included in the relationships because of a lack of field data. Based on the knowledge obtained in this study, the following recommendations for further work are made:

1. The development of modified relationships for K_L to include wind velocity through the dimensional analysis procedure, is recommended.
2. It is recommended to test the applicability of the relationships to chemical compounds other than ethylene as data become available.
3. Detailed field data collection, including the channel hydraulic parameters (discharge, width, depth, velocity, bed slope) and wind velocity measurement, are recommended to be undertaken in future studies on volatilization of organic compounds of public health concern from natural water bodies.
4. Investigation of relationships between K_L and molecular properties for chemical compounds with Henry's constants lower than 10^{-3} atm - m³/mol (i.e., moderate and low volatile compounds) is recommended.

REFERENCES

- Arbuckle, W.B., 1983. Estimating Activity Coefficients for Use in Calculating Environmental Parameters, *Environ. Sci. Technol.*, 17: 537-542.
- Bacchus, A., 1981. Field Measurement of Stream Reaeration Coefficient. Water Resources Paper 13, Ontario Ministry of the Environment, Toronto.
- Banerjee, S., Yalkowsky, S.H. and Valvani, S.C., 1980. Water Solubility and Octanol/Water Partition Coefficients of Organics. Limitations of the Solubility-Partition Coefficient Correlation. *Environ. Sci. Technol.*, 14: 1227-29.
- Chiou, C.T. and Freed, V.H., 1977. Chemodynamic Studies on Benchmark Industrial Chemicals, MSF/RA-770286. MTIS PB 274263.
- Chiou, C.T. and Freed, V.H., 1979. Evaporation Rates from Single Component and Multicomponent Systems, Preprints of Papers Presented at the 177th National Meeting, Honolulu, Hawaii, April 1-6, 1979, American Chemical Society, Division of Environmental Chemistry, 19, No. 1.
- Cohen, Y., Cocchio, W. and Mackay, D., 1978. Laboratory Study of Liquid-Phase Controlled Volatilization Rates in Presence of 2 Wind Waves. *Environ. Sci. Technol.*, 12: 553-58.
- Dean, J.A. (Ed.), 1979. Lange's Handbook of Chemistry, 12th edition, McGraw-Hill Book Co., New York.
- Dilling W.G., 1977. Interphase Transfer Processes, II. Evaporation Rates of Chloro Methanes, Ethanes, Ethylenes, Propanes and Propylenes from Dilute Aqueous Solutions. Comparison with Theoretical Predictions. *Environ. Sci. Technol.*, 11(4): 405-409.
- Fishtine, S.H., 1963. Reliable Latent Heats of Vapourization. *Industrial and Engineering Chemistry*, 55:47.
- Hansch, C. and Leo, A.J., 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. John Wiley, New York.
- Hayduk, W. and Laudie, H., 1974. Prediction of Diffusion Coefficients for Non-Electrolysis in Dilute Aqueous Solutions. *AIChEJ.*, 20: 611-15.
- Kaczmar, S.W., D'Itri, F.M. and Zabik, M.J., 1984. Volatilization Rates of Selected Haloforms from Aqueous Environments. Short Communication. *Environmental Toxicology and Chemistry*, 3: 31-35.
- Lewis, W.K. and Whitman, W.G., 1924. Principles of Gas Absorption. *Industrial and Engineering Chemistry*, 16 (12): 1215-1220.
- Liss, P.S. and Slater, P.G., 1974. Flux of Gases Across the Air-Sea Interface. *Nature*, 247: 181-184.
- Lyman, W.J., Reehl, W.F. and Rosenblatt, D.H. (eds), 1982. Handbook of Chemical Property Estimation Methods - Environmental Behaviour of Organic Compounds. McGraw-Hill Book Co., Toronto.

- Mackay, D. and Wolkoff, A.W., 1973. Rate of Evaporation of Low Solubility Contaminants from Water Bodies to Atmosphere, *Environ. Sci. Technol.*, 7: 611-14.
- Mackay, D. and Leinonen, P.J., 1975. Rate of Evaporation of Low Solubility Contaminants from Water Bodies to Atmosphere. *Environ. Sci. Technol.*, 9: 1178-1180.
- Mackay, D., Shiu, W.Y. and Sutherland, R.P., 1979. Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants. *Environ. Sci. Technol.*, 13: 333-337.
- Mackay, D. and Yuen, T.K., 1980. Volatilization Rates of Organic Contaminants from Rivers. *Water Pollution Research Journal of Canada*, 15 (1): 83-98.
- Mackay, D. and Yuen, T.K., 1983. Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water. *Environ. Sci. Tech.*, 17 (4): 211-217.
- McCarty, P.L., 1980. Organics in Water - An Engineering Challenge. *J. of the Environmental Engineering Division, ASCE*, 106 (EE1): 1-17.
- Meissner, H.P., 1949. Critical Constants from Parachor and Molar Refraction. *Chem. Eng. Prog.*, 45: 149-153.
- Mumford, S.A. and Phillips, J.W.C., 1928. Observations on the Chlorination Products of β,β -Dichlorodiethyl Sulphide. *J. Chem. Soc.*, 155-162.
- Mumford, S.A. and Phillips, J.W.C., 1929. The Evaluation and Interpretation of Parachors. *J. Chem Soc.*, 2112-2133.
- Perry, R.H. and Chilton, C.H. (eds)., 1973. *Chemical Engineers' Handbook*, 5th edition, McGraw-Hill Book Co., New York.
- Quayle, O.R., 1953. The Parachors of Organic Compounds: An Interpretation and Catalogue. *Chem. Rev.*, 53: 439-589.
- Rainwater, K.A. and Holley, E.R., 1984. Laboratory Studies on Hydrocarbon Tracer Gases. *Journal of the Environmental Engineering, ASCE*, 110(1): 27-41.
- Rathbun, R.E. and Tai, D.Y., 1981. Technique for Determining the Volatilization Coefficients of Priority Pollutants in Streams, *Water Research*, 15: 243-250.
- Rathbun, R.E. and Tai, D.Y., 1982. Volatilization of Organic Compounds from Streams. *Journal of the Env. Eng. Div., ASCE* 108 (EE5): 973-989.
- Rathbun, R.E., Shultz, D.J., and Stephens, D.W., 1975. Preliminary Experiments with a Modified Tracer Technique for Measuring Stream Reaeration Coefficients. United States Department of the Interior Geological Survey Open File Report No. 75-256, Bay St. Louis, Mississippi.
- Rathbun, R.E., Stevens, D.W., Shultz, D.J., and Tai, D.Y. 1978. Laboratory Studies of Gas Tracers for Reaeration. *Journal of Environmental Engineering Division, ASCE*, 104(EE2): 215-229.
- Reid, R.C., Prausnitz, J.M. and Sherwood T.K., 1977. *The Properties of Gases and*

Liquids, 3rd ed., McGraw-Hill Book Co., New York.

- Roberts, P.V. and Dandliker, P.G., 1983. Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere during Surface Aeration. *Environ. Sci. Technol.*, 17(8): 484-489.
- Rouse, H., 1961. Fluid Mechanics for Hydraulic Engineers. Dover Publications Inc., New York.
- Sax, N.I., 1979. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Co., Toronto.
- Smith, J.H. and Bomberger, D.C., 1978. Prediction of Volatilization Rates of Chemicals in Water, *Water: 1978 AIChE Symposium Series*, 190: 75: 375-81.
- Smith, J.H., Bomberger, D.C. and Haynes, D.S., 1980. Prediction of the Volatilization Rates of High Volatility Chemicals from Natural Water Bodies. *Environ. Sci. Technol.*, 14: 1332-37.
- Southworth, G.R., 1979. The Role of Volatilization in Removing Polycyclic Aromatic Hydrocarbons from Aquatic Environments. *Bull. Environ. Contam. Toxicol.*, 21: 507-514.
- Thomson, G.W., 1959. Determination of Vapour Pressure. In *Techniques of Organic Chemistry*, ed. A. Weissberger, 3rd ed., Vol 1, Part 1, Interscience, New York, p. 473.
- Tsivoglou, E.C., 1967. Tracer Measurements of Stream Reaeration. Federal Water Pollution Control Administration, Washington, D.C. NTIS PB 229923/BA.
- Verschueren, K., 1977. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Co., New York.
- Weast, R.C. and Astle, M.J. (eds)., 1980-81. Handbook of Chemistry and Physics, 60th ed., CRC Press, Inc., West Balm Beach, Florida.

APPENDIX

COMPOUNDS OF HIGH VOLATILITY

	$\frac{H^a}{\text{atm m}^3/\text{mol}}$	$\frac{P}{\text{atm}}$	$\frac{C_s}{\text{mol/m}^3}$	<u>Other Data</u>
<u>Hydrocarbons</u>				
Benzene	4.4×10^{-3} (1)			
Butylene	$> 10^{-3}$ (7)			
Cyclohexane	0.15	0.10 (5)	0.65 (5)	
Ethylene	> 8.6	> 40 (4)	4.7 (4)	
Ethylbenzene	8.7×10^{-3}	1.25×10^{-2} (4)	1.43 (4)	
	5.7×10^{-3} (6)			
Isopropylbenzene	9.8×10^{-3} (5)	4.2×10^{-3} (5)	0.42 (5)	
n-Hexane	1.4	0.16 (5)	0.11 (5)	
Natural gas	$>> 10^{-3}$ (7)			
Propylene	2.1×10^{-3}	10 (12)	4.75 (5)	
Styrene (monomer)	4.3×10^{-3} (5)	6.6×10^{-3} (9)	1.54 (9)	
Toluene	5.2×10^{-3} (1)			
	5.7×10^{-3} (6)			
	6.6×10^{-3} (4)	3.7×10^{-2} (4)		

Xylene

ortho	5.3×10^{-3} @ 25 C	8.7×10^{-3} @ 25 C (3)	1.64 @ 25 C (3)
meta	4.2×10^{-3} (7)	7.9×10^{-3} (5)	
para	4.6×10^{-3}	8.6×10^{-3} (5)	1.87 (5)

Polycyclic Aromatic Hydrocarbons (PAHs)

Anthracene	1.4×10^{-3} (6)
Naphthalene	1.18×10^{-3} (4)

Oxygenated Hydrocarbons

Pesticides

Aldrin	2.1×10^{-3} (6)
alpha-Hexachlorocyclohexane	2.0×10^{-3} (6)
Toxaphene	6.3×10^{-2} (6)

Halogenated Hydrocarbons

Bromomethane (methyl bromide)	0.25	2.4 (5)	9.5 (5)
Carbon Tetrachloride	2.5×10^{-2} (6)		
Chlorobenzene	2.6×10^{-3} (1)		
	4.0×10^{-3} (6)		
Chloroethane	1.5×10^{-2} (6)		

Chloroform	3.4×10^{-3} (6)		
Chloromethane	31	5.0 (5)	0.16 (5)
3-Chloropropene	1.1×10^{-2} (10)		
1,2-Dichlorobenzene	1.7×10^{-3} (6)		
1,3-Dichlorobenzene (m-dichlorobenzene)	2.7×10^{-3} (6)		
1,4-Dichlorobenzene (p-dichlorobenzene)	2.1×10^{-3} (6) 3.4×10^{-3} (9)		
Dichlorodifluoromethane	2.4	5.6 (5)	2.3 (5)
1,1-Dichloroethane	5.1×10^{-3} (6)		
1,1-Dichloroethene (vinylidene chloride)	1.7×10^{-1} (6)		
cis-1,2-Dichloroethene	7.5×10^{-3} (10)		
trans-1,2-Dichloroethene	6.5×10^{-3} (10)		
1,2-Dichloropropane	2.1×10^{-3} (1)		
Hexachloroethane	1.1×10^{-3} (6)		
Methylene chloride	3.0×10^{-3} (4)	0.46 (4)	155 (4)
PCBs			
Aroclor 1248	3.51×10^{-3} (3)		
Aroclor 1254	2.76×10^{-3} (3)		
Aroclor 1260	7.13×10^{-3} (3)		
Pentachloroethane	-2.4×10^{-3} (10)		

Perchloroethylene (tetrachloroethene)	8.3×10^{-3} (4)	2×10^{-2} (4)	2.4 (4)
1,1,1,2-tetrachloroethane	2.6×10^{-3} (10)		
1,1,1-Trichloroethane	1.8×10^{-2} (4) 3.6×10^{-3} (6)		
Trichloroethene	1.0×10^{-2} (6)		
Trichlorofluoromethane	0.11 (6)		
2,3 Dichloropropene	3.6×10^{-3} (10)		
cis-1,3-Dichloropropene	2.3×10^{-3} (10)		
trans-1,3-Dichloropropene	1.7×10^{-3} (10)		
Vinyl chloride (chloroethene)	2.4 (4) 6.4 (6)	3.4 (4)	1.44 (4)

Nitrogen Compounds

Methylamine	8.3×10^{-2}	3.1 (5)	37.2 (5)
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Miscellaneous Compounds

Carbon disulfide	1.1×10^{-2}	0.34 (5)	30.2 (5)
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COMPOUNDS OF MODERATE VOLATILITY

Hydrocarbons

Acetylene	7.5×10^{-4} (7)	40 (5)	
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1,3-Butadiene	2.4×10^{-4}	3.3×10^{-3} (5)	13.6 (5)
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Polycyclic Aromatic Hydrocarbons (PAHs)

Benzo(a)pyrene	1.3×10^{-6} (11)
Acenaphthene	1.9×10^{-4} (6)
Fluorene	2.1×10^{-4} (6)
Phenanthrene	1.3×10^{-4} (6)

Oxygenated Hydrocarbons

Acetone	1.5×10^{-5} (7)		
Acrolein	9.7×10^{-5} (6)		
n-Butanol	5.6×10^{-6}	5.8×10^{-3} (5)	1040 (5)
n-Butyraldehyde	$1.0 \text{ to } 2.2 \times 10^{-4}$ (7)		430 to 985 (5)
Cresols			
ortho	1.1×10^{-6} (7)		
meta	2.4×10^{-7} (7)	5.3×10^{-5} (5)	
para	8.6×10^{-6} (11)		
Dimethyl ether	3.3×10^{-4} (7)	5.0 (12)	
Dimethyl phthalate	4.2×10^{-7} (6)		
4,6-Dinitro-o-cresol	1.7×10^{-7} (6)		
Ethylene Oxide	7.7×10^{-5} (7)	1.4 (5)	

2-Ethylhexanol	2.1×10^{-5} (7)	3.1 (5)	
Isophorone	5.8×10^{-6}	5.0×10^{-4} (5)	87 (5)
Isopropanol	9.3×10^{-6} (7)	4.2×10^{-2} (5)	
Methyl Ethyl Ketone	2.0×10^{-5}	0.10 (5)	4900 (5)
Methyl Isobutyl Ketone	4.7×10^{-5}	7.9×10^{-3} (5)	170 (5)
2-Nitrophenol	7.6×10^{-5} (6)		
Pentachlorophenol	3.4×10^{-6} (4)	1.8×10^{-7} (4)	5.3×10^{-2} (4)
Phenol	2.7×10^{-7} (6)		
Vinyl Acetate	3.8×10^{-4}	1.1×10^{-1} (5)	290 (5)

Pesticides

Chlordane	3.7×10^{-4} (7)
DDT (4,4'-DDT)	3.4×10^{-5} (6)
Dieldrin	1.7×10^{-7} (6)
Lindane	3.2×10^{-7} (6)
Methyl parathion	7.8×10^{-5} (11)
Mirex	1.9×10^{-4} (11)

Halogenated Hydrocarbons

Bis(2-chloroethyl)ether	1.3×10^{-5}	9.3×10^{-4} (5)	71.3 (5)
Bis(2-chloroisopropyl)ether	1.1×10^{-4} (6)		

1,2-Dichloroethane	9.6×10^{-4} (10)		
Ethylene Dibromide	6.6×10^{-4} (4)		
PCBs			
Aroclor 1242	4.9×10^{-4} (6)		
Tribromomethane	5.9×10^{-4}	7.4×10^{-3} (5)	12.6 (5)
1,2,3-Trichloropropane	3.1×10^{-4} (10)		
1,1,2,2-Tetrachloroethane	4.2×10^{-4} (6)		
1,1,2-Trichloroethane	7.8×10^{-4} (6)		

Nitrogen Compounds

Acrylonitrile	6.3×10^{-5} (6)		
Ammonia	2.7×10^{-4}	8.7 (5)	32000 (5)
Carbazole	1.6×10^{-4} (11)		
Nitrobenzene	1.1×10^{-5} (6)		
Hydrazine	1.8×10^{-5} (7)	2.1×10^{-2} (5)	

Miscellaneous Compounds

Benzo(b)thiophene	2.7×10^{-4} (11)
Dibenzothiophene	4.4×10^{-4} (11)

COMPOUNDS OF LOW VOLATILITY

Polycyclic Aromatic Hydrocarbons (PAHs)

Benz(a)anthracene 1.3×10^{-7} (11)

Oxygenated Hydrocarbons

Ethanol $< 10^{-7}$ 5.8×10^{-2} (5)

Ethanolamine 9.1×10^{-8} (7) 5.3×10^{-4} (5)

Ethylene glycol $<< 10^{-7}$ 6.6×10^{-5} miscible

Methanol $<< 10^{-7}$ 1.2×10^{-1} miscible

Nitrogen Compounds

Benzo(f)quinoline 9.5×10^{-9} (11)

E-Caprolactam 2.6×10^{-10} (7) 1.3×10^{-6} (5)

Dibenzo(c,g)carbazole 4.7×10^{-9} (11)

Morpholine 4×10^{-8} (7) 1.1×10^{-2} (5)

Urea $< 10^{-7}$ (7)

Nitroglycerine 4.1×10^{-8} (7)

Quinoline

2.5×10^{-7} (11)

a: For 20°C unless otherwise noted

1. Mackay and Yuen (1983)
2. Banerjee et al (1980)
3. Mackay and Leinonen (1975)
4. Mackay et al (1979)
5. Verchueren (1977)
6. McCarty (1980) calculated values
7. P_c and/or C_s estimated using the methods of Chapter 5
8. Sax (1979) ^s
9. Arbuckle (1983)
10. Dilling (1977); some values were estimated. See reference for details
11. Smith and Bomberger (1978)
12. Weast and Astle (1980-81)

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